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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on pages 3 and 4 of the JOURNAL cover. New tables will be announced from time to time as they become available. An order blank is available on the last page of this issue.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1688

Part of Journal of Research of the National Bureau of Standards, Volume 36, January 1946

SPECIFICATION OF RAILROAD SIGNAL COLORS AND GLASSES

By Kasson S. Gibson, Geraldine Walker Haupt, and Harry J. Keegan

ABSTRACT

This paper is a continuation of Bureau Research Paper RP1209 and describes the cooperative work done by the Association of American Railroads Signal Section, Corning Glass Works, and the National Bureau of Standards leading to the formulation of the AAR Signal Section specifications for signal colors and glasses.

The previous paper defined the luminous transmission scale used by the signal engineers and glass manufacturers. The present paper describes the glasses selected by these engineers to define the limits of acceptable chromaticities afforded by these glasses when combined with kerosine* or electric illuminant. The spectral transmissions of the glasses are given, together with the luminous transmissions and chromaticities for the specified illuminants.

The photometric and colorimetric parts of the AAR Signal Section three-part specifications are illustrated and the reasons given for the choice of tolerances both on the acceptable signal colors and on the glasses certified by the National Bureau of Standards as duplicates of the standard limit glasses.

Various other data of interest are given, including the expression of the permissible chromaticities of signal colors in a uniform-chromaticity-scale coordinate system.

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I. INTRODUCTION

This is the second paper describing the work of the National Bureau of Standards on the color standardization of railroad signal glasses. This standardization has resulted from the cooperative efforts of the Signal Section of the Association of American Railroads (formerly the American Railway Association), Corning Glass Works, and the National Bureau of Standards.

The first paper [1] gave a historical résumé of signal-color activities

*In this paper, except for quoted matter and publication titles, the spellings "kerosine" and "disk" are used consistent with Bureau practice.

[1] Kasson S. Gibson and Geraldine Walker Haupt, Standardization of the luminous-transmission scale used in the specification of railroad signal glasses, J. Research NBS 22, 627 (1939) RP1209; J. Opt. Soc. Am. 29, 188 (1939).

of the AAR Signal Section with particular reference to the specifications issued by that organization (or its precursors) in 1908, 1918, and 1935. Various acknowledgments and references to previous work were also given, which are not repeated here.

The principal purpose of the previous paper was to describe the methods and data used in the derivation of the luminous-transmission scale now used by the signal engineers and to express that scale on a fundamental, absolute basis. The end result of that work is given in table 1, which is a transcription of table 7 of the earlier paper.

TABLE 1.—*Relation between values of T_{AAR} and of $T_{2,360}$, which defines the luminous transmission scale used in the present AAR signal-glass specifications*

Color designation of glass	AAR transmission, T_{AAR}	Equivalent luminous transmission, 1931 ICI standard observer, illuminant 2,360° K, $T_{2,360}$	Color designation of glass	AAR transmission, T_{AAR}	Equivalent luminous transmission, 1931 ICI standard observer, illuminant 2,360° K, $T_{2,360}$
Red	100.0	0.069	Blue	100.0	0.0223
Yellow	100.0	.247	Purple	100.0	.0129
Green	100.0	.119	Lunar white	100.0	.190

It may be seen that for each of the six signal colors used by the railroad engineers—designated by them as red, yellow, green, blue, purple, and lunar white—the luminous transmissions of glasses are expressed on an arbitrary scale with the symbol T_{AAR}. The expression of that scale (in reality six scales, a different one for each color) on an absolute basis with illuminant at 2,360° K is given in table 1.

The purpose of the present paper is to consider the chromaticities of railroad signal colors and glasses. The parts of the 1908 and 1918 specifications dealing with chromaticity are noted, the glasses newly selected by the signal engineers (beginning in 1931) to define the limits of permissible colors are listed and their spectral and luminous transmissions given, the methods used to express the results in colorimetric terms suitable for specification purposes are described, and pertinent parts of the current railroad signal specifications are quoted and illustrated.

The work covered in these two papers, and many other details of the investigation, may be found in seven formal reports issued to the cooperating agencies during the period 1932 to 1938.[2]

[2] Standardization of railway signal glasses—Reports on measurements and investigations undertaken by the Colorimetry Section of the National Bureau of Standards at the request of the Signal Section, American Railway Association.

Reports 1 to 5, Signal Section Proc., Am. Ry. Assn. **30**, 384 (1933):

Report 1. K. S. Gibson. The transmission (ARA scale) of 36 specimens of signal glass relative to transmission of 6 ARA standards marked "J. C. Mock 10-3-30," a report on measurements made at Corning Glass Works, December 9-11, 1930 (June 1, 1932).

Report 2. K. S. Gibson and Geraldine K. Walker, Measurements of spectral and luminous transmissions leading to the derivation of new ARA transmissions for the 36 glasses listed in report 1 (October 24, 1932).

Report 3. Geraldine K. Walker and K. S. Gibson, Spectral and luminous transmissions and derivation of new values of ARA transmission for the 22 "limit" glasses selected by committee VI, ARA, at Corning, November 5-6, 1931, and engraved "J. C. M. 11-6-31" (December 2, 1932).

Report 4. K. S. Gibson and Geraldine K. Walker, Chromaticities and luminous transmissions, with illuminants at 1,900° K and 2,848° K, for the 22 "limit" glasses described in report 3 (January 30, 1933).

Report 5. K. S. Gibson, Tentative specifications for railway signal colors (April 27, 1933).

Reports 6 and 7, K. S. Gibson, Geraldine Walker Haupt, and H. J. Keegan, Signal Section Proc., Assn., Am. R. R. **36**, 126 (1939):

Report 6. Examination of 65 duplicate limit glasses (July 26, 1934).

Report 7. Colorimetric data leading to specification 59-38 for kerosene hand lantern globes; comparison of specifications 59-38, 60-38, and 60-35; certification of duplicate lantern glasses (September 28, 1938).

II. METHODS USED TO SPECIFY THE CHROMATICITIES OF RAILROAD SIGNAL COLORS AND GLASSES

Workers in colorimetry have become so familiar with the methods of computation and specification in terms of the 1931 ICI Standard Observer and Coordinate System for Colorimetry that discussion and explanations are often no longer needed. This has only recently been true, however, and at the times of issue of the 1908 and 1918 railroad signal glass specifications [3] little knowledge and no convenient computational procedures were available for such work. Furthermore, the art of spectrophotometry had not progressed sufficiently, at least in 1908, to warrant the precise colorimetric standardization that has become commonplace in recent years.

It was noted in the previous paper that a chromaticity (mixture) diagram, so essential in specifying the chromatic properties of signal lights, had been illustrated in colors and used by Dr. Churchill in 1905 in his study of the characteristics of signal glassware.[4] No attempt was made, however, in either the 1908 or 1918 specification to use a method of specification based on such a system. Instead, are found the following qualitative restrictions expressed in terms of spectral hues:

Excerpts from 1908 Railway Signal Association Specifications for Signal Roundels and Lenses

Red.—Will be of such quality that all yellow rays of light are absorbed, the spectrum being either red, or red and orange. The photometric value shall be, light 125, standard 100, dark 75.

Green.—Will be of the color known as admiralty green, having a slightly bluish tint. The spectrum shall show very little yellow, being a full green with some blue. The photometric value shall be, light 125, standard 100, dark 75.

Yellow.—Will give a spectrum showing a full yellow band, most of the red and slightly of the green. The photometric value shall be, light 120, standard 100, dark 80.

Blue.—Will give a spectrum having a full blue band, with a narrow band of green. The photometric value shall be, light 125, standard 100, dark 75.

Purple.—Will give a spectrum showing a considerable proportion of both red and blue. The photometric value shall be, light 125, standard 100, dark 75.

Lunar White.—Shall show a maximum of absorption for the yellow. The photometric value shall be, light 120, standard 100, dark 80.

The scales on which the photometric values of the 1908 and 1918 specification are based are roughly as defined in table 1. This is discussed in the previous paper.

Excerpts from 1918 Railway Signal Association Specification 6918 for Signal Roundels, Lenses and Glass Slides

Red.—Shall be of such quality that all yellow rays of light emitted by the sodium flame are absorbed, the spectrum being either red, or red and orange.

Green.—Shall be of the color known as admiralty green, having a slightly bluish tint as seen in daylight. The spectrum shall show most of the blue and green, a slight amount of yellow, and not more than a trace of orange and red.

Yellow.—Shall give a spectrum showing most of the red, all of the yellow, and part of the green, but no blue.

[3] Specifications for signal roundels, lenses, and glass slides, Proc. Ry. Signal Assn. 5 (1908). Railway Signal Association specification 6918, Signal roundels, lenses, and glass slides (1918).

[4] Wm. Churchill, The roundel problem. A paper presented at the Ninth Annual Meeting of the Railway Signal Association, Nagrara Falls, N. Y., October 10-12, 1905.

Blue.—Shall give a spectrum showing most of the blue, some green, and almost no red.

Purple.—Shall give a spectrum showing most of the blue, some green, and a narrow band of the extreme red.

Lunar White.—Shall show blue and green, with about ten (10) percent of yellow and orange, and some red. It shall appear a light blue when viewed by daylight, and when placed in front of a yellow kerosene flame, it shall make this flame appear white.

In addition, in the 1918 specification there is given a table showing the light and dark limits for each of the six colors: red 160 to 100, green 175 to 125, yellow 140 to 100, blue 125 to 75, purple 125 to 75, and lunar white 120 to 80.

While it is obvious, therefore, that chromaticity limits were not given as such in either specification, the light and dark limits were apparently tacitly used as chromaticity limits. This, combined with the spectral restrictions noted above, served with considerable effectiveness to protect American railroads against signal glassware outside the chosen chromaticity and transmission ranges. It was noted in the previous paper that the 1908 specification appears to have been the first effort in this country to place the colorimetric part of a purchase specification on a fundamental basis, the specification being based on spectrophotometric data and establishing tolerances within which the manufactured product must come.

During the 1920's great advances were made in colorimetry. In 1922 the Optical Society of America Colorimetry Committee published a report [5] giving data and computational procedures for deriving and specifying the chromaticity of a color based on spectrophotometric data. In 1924, standard luminosity factors [6] were adopted by the International Commission on Illumination, in terms of which the intensities of colored lights and the luminous transmissions of signal glasses may be expressed. In 1931 the International Commission on Illumination adopted data defining a standard observer and coordinate system for colorimetry,[7] which has become the recognized method for specifying color. It incorporates the standard luminosity factors. The computational procedure, operating on spectrophotometric data, results in coordinates serving to specify the chromaticity of a color. In this coordinate system, x, y, and z represent fractional parts of hypothetical reddish, greenish, and bluish primaries ($x+y+z=1$), and it is customary to express the chromaticity diagram in terms of x and y. This system is now well known and widely used, and the reader is referred to the other publications listed for further information.

Along with this advance in colorimetry there occurred further progress in the manufacture of signal glassware. The status of this work was summarized by Gage in 1928. [8]

In 1930 was initiated the program in which the AAR Signal Section, Corning Glass Works, and the National Bureau of Standards have

[5] Optical Society of America Committee on Colorimetry, L. T. Troland, chairman, Report for 1920-21, J. Opt. Soc. Am. & Rev. Sci. Instr. **6**, 527 (1922).

[6] Proceedings Sixth Meeting Int. Comm. Illum., Geneva, p. 67 (1924). For a résumé of recent work and the present status of these ICI luminosity factors, see K. S. Gibson, Spectral luminosity factors, J. Opt. Soc. Am. **30**, 51 (1940).

[7] Proceedings Eighth Meeting, Int. Comm. Illum., Cambridge, p. 19 (1931).
D. B. Judd, The 1931 ICI standard observer and coordinate system for colorimetry, J. Opt. Soc. Am. **23**, 359 (1933).
A. C. Hardy, Handbook of colorimetry, Technology Press, Cambridge, Mass. (1936).
Optical Society of America, Committee on Colorimetry, Quantitative data and methods for colorimetry, J. Opt. Soc. Am. **34**, 633 (1944); chapter VII of the forthcoming OSA Colorimetry Committee report.

[8] H. P. Gage, Practical considerations in the selection of standards for signal glass in the United States, Proc., Int. Cong. Illum., Saranac Inn, N. Y., p. 834 (1928).

cooperated, as described in the previous paper. In 1931 the railroad signal engineers selected a completely new set of standard glasses explicitly defining new limits of chromaticity for the respective colors. As a result of the work thus started, new AAR Signal Section specifications have appeared during the years 1935 to 1940.[9] The colorimetric parts of these specifications are expressed entirely in the fundamental terms of the 1931 ICI standard observer and coordinate system. Here, as before, the signal engineers have been pioneers in the use of color specifications. It is believed that the suggested "Specification for railway signal colors" appearing in the 1933 Signal Section Proceedings and including a chromaticity (x, y) diagram (similar to fig. 8), on which are plotted points representing the standard glasses and areas representing permissible chromaticities for the six signal colors, is the first published use of the ICI colorimetric system for specification purposes.[10] Methods similar to this have since been followed in specifying the colors and glasses used in traffic, marine, and aviation signaling, both here and abroad.[11]

III. STANDARD GLASSES DEFINING LIMITS OF ACCEPTABLE CHROMATICITIES FOR RAILROAD SIGNAL COLORS.

At a meeting held at Corning Glass Works on November 5 and 6, 1931, numerous glasses were selected to define the new limits of acceptable chromaticities which it was desired to standardize. These glasses were selected by members of Committee VI of the AAR Signal Section, J. C. Mock, chairman. During the course of the work a few of the glasses were superseded by others. As a group they comprise the standards covering the use of roundels, lenses, slides (pressed ware), and disks for railroad signaling, and are designed for use with electric (incandescent) and/or kerosine illuminants. They include the colors designated as red, yellow, green, blue, purple, and lunar white.

At a meeting of Subcommittee C of Committee VI, A. S. Haigh, chairman, held at Corning Glass Works in June 1935, additional glasses were selected, representing the chromaticity limits for red, yellow, green, and blue kerosine hand lantern globes, and in 1939 the limits for highway-crossing red were likewise selected.

It may be noted that all of these standard limit glasses were selected by experienced signal engineers as a result of field tests conducted at Corning Glass Works. Final selection was based both on the desired differentiation of signals of the various colors and on reasonable manufacturing tolerances required for each of the colors. Numerous details may be found in the seven published reports from the National Bureau of Standards (see footnote 2, p. 2) and in the Proceedings of the

---

[9] Specification 69 is entitled "Signal glasses (exclusive of kerosene hand lantern globes)." It was published in essentially its present form in 1935, and was designated as 69–35. Slightly revised editions were published in 1938, 1939, and 1940, 69–40 being the current specification. Similarly, specification 59, "Kerosene hand lantern globes," was published in essentially its present form in 1938, the current edition being designated 59–39. Copies of these specifications are obtainable from R. H. C. Balliet, Secretary, AAR Signal Section, 30 Vesey St., New York, N. Y.

[10] K. S. Gibson, Report 5, Tentative specifications for railway signal colors, Signal Section Proc., Am. Ry. Assn. 30, 429 (1933).

[11] See, for example, (1) Standards of the Institute of Traffic Engineers, Technical Report No. 1, Adjustable face traffic control signal head standards, 1940 Proceedings, (2) Bureau of Marine Inspection and Navigation (now part of U. S. Coast Guard), Proposed specification covering navigation lights for vessels, alteration D (1941), (3) Army-Navy Aeronautical Specification: Colors; aeronautical lights and lighting equipment; AN–C–56 (1942); (4) Proceedings Int. Comm. Illum., Tenth Session, Scheveningen, Holland (1939), condensed unofficial version edited and published by the United States National Committee, figure 17.

AAR Signal Section, to which reference is made in the previous paper. These standard limit glasses have all been deposited with the National Bureau of Standards.

A description of the glasses finally selected as standards (and in current use) is given in table 2.[12] Their spectral transmissions are given in table 3.

In table 4 are given (1) the chromaticity coordinates and luminous transmissions of each glass in combination with the illuminants of color temperatures 1,900°, 2,360°, and 2,848° K, (2) the T_{AAR} value for each glass, and (3) the ratio of red to total luminous transmission, T_r/T_w, for the blue and purple glasses for 2,360° K. The values given in table 4 are all uncertain in the last figure given; this uncertainty relates to uncertainties in the spectral transmissions in table 3 and to rejection errors or other factors in the methods of computation. In some cases this uncertainty may extend slightly into the next to last figure. Values of T_{AAR} are derived from values of $T_{2,360}$ by conversion factors carried to one more significant figure than given in table 1.

The spectral transmissions given in table 3 are illustrated in figures 1 to 6. The values of x and y given in table 4 are plotted in the charts illustrating the final specifications, figures 8 and 9. Various data on certain of the superseded limit glasses are given in the several Bureau published reports to which references have already been made.

The spectral transmissions given in table 3 were determined mostly on the König-Martens visual spectrophtometer [13] and the Gibson photoelectric spectrophotometer.[14] Measurements were made usually at every 10 mμ from 380 to 770 mμ, the photoelectric measurements extending usually from 380 to 500 mμ and from 660 to 770 mμ, and the visual measurements from somewhere in the range 450 to 500 mμ to somewhere in the range 680 to 720 mμ, in addition to the mercury wavelengths 404.7 and 435.8 mμ. The values adopted and given in table 3 are usually uncertain in the last figure. All the curves in figures 1 to 6 are typical with one exception. This exception is the curve for red-limit disk yellow 200, figure 2. Glasses 199 and 200 are of the type known as selenium yellows, characterized usually by the high transmission in the red, orange, and yellow, essentially complete absorption in the blue and violet, and sharp transition in the green or yellow green. Occasionally, however, a melt is obtained with an "unsharp cut-off," as it is usually called, and glass 200 is a good example. Note the transmission extending in measurable amounts through the blue and violet.

Glass 200 had been selected and marked as standard before it was suspected that it failed to be typical. The fact that the failure was not detected by inspection shows that it is not of much importance. However, the value of the blue coordinate, z, is larger than normal and affected the tolerance established for such glasses, as is illustrated in figure 11.

[12] In describing these glasses the expressions "light limit" and "dark limit" have been retained because of their widespread use among signal engineers and glass manufacturers. The term "dark limit" is more or less appropriate, but the term "light limit" is inappropriate, as there is no upper limit of luminous transmission placed on any glassware in the specifications. The "light limit" glasses all define chromaticity limits, as indicated in table 2. Likewise, the values of T_{AAR} are given in the table because of their widespread usage in describing signal glasses.

[13] H. J. McNicholas, Equipment for routine spectral transmission and reflection measurements, BS J. Research **1**, 793 (1928) RP30.

[14] K. S. Gibson, Direct-reading photoelectric measurement of spectral transmission, J. Opt. Soc. Am. & Rev. Sci. Instr. **7**, 693 (1923).

TABLE 2.—*Description of glasses selected by AAR Signal Section Committee VI as defining the chromaticity limits of railroad signal colors*

TABLE 2.—*Description of glasses selected by AAR Signal Section Committee VI as defining the chromaticity limits of railroad signal colors*

Color designation	Type	Photometric designation	Number of glass	Values of T_{AAR}	Chromaticity limit	Designed for illuminant	Remarks
AAR SIGNAL SECTION SPECIFICATION 69-40							
Red	Except highway crossing	Light	154	177.0	Pale and yellow	Electric, E, and Kerosine, K.	For pressed ware and disks, heat resisting, HR.
		Dark	86	102.9	(a)		
Do	Highway crossing	Light	75	288.2	Pale and yellow	E	For pressed ware, HR.
		Dark	400	217.6	(a)		
Yellow	Non-HR	Light	141	214.1	Pale and green	E and K	For pressed ware.
		Dark	142	160.8	Red		
Do	Disk	(e)	199	270.5	Pale and green	E	For disks, HR.
			200	251.0	Red		
Green	Non-HR	Light	134	205.9	Pale and yellow	E and K	For pressed ware.
		Dark	87	150.5	Blue		
Do	Disk	Light	139	193.4	Pale and yellow	E	For disks, HR.
		Dark	140	138.7	(b)		
Blue	Non-HR	Light	47	130.2	Pale and green	E and K	For pressed ware.
		Dark	57	74.7	Red		
Purple	Kerosine	Light	56	131.2	Pale and green [c]	K	For pressed ware, non-HR.
		Dark	47	73.3	Red [c]		
Do	Electric	Light	80	40.1	Pale and green [c]	E	For disks, HR.
		Dark	108	30.3	Red [c]		
Lunar white	Kerosine	Light	45	121.7	Yellow [d]	K	For pressed ware, non-HR.
		Dark	74	79.6	Blue [d]		
Do	Electric	Light	124	205.3	Yellow [d]	E	For disks, non-HR.
		Dark	73	146.6	Blue [d]		
AAR SIGNAL SECTION SPECIFICATION 59-39							
Red	Kerosine lantern	Light	201	256.7	Pale and yellow	K	For hand lantern globes, HR.
		Dark	211	145.5	(a)		
Yellow	do	Light	261	297.4	Pale and green	K	For hand lantern globes, HR.
		Dark	271	241.2	Red		
Green	do	Light	137	184.9	Pale and yellow	K	For hand lantern globes, HR.
		Dark	322	126.6	Blue		
Blue	do	Light	141	124.8	Pale and green	K	For hand lantern globes, HR.
		Dark	131	86.0	Red		

[a] No chromaticity limit is needed. The dark limit glass is useful, however, in the photometry of red signal glassware.
[b] Non-HR green No. 87 has been accepted as the blue limit for disk greens.
[c] These chromaticity limits have little significance. The purple glass gives a dichromatic signal, and the ratio of red to blue (or total) light is the important criterion.
[d] Green and purple limit glasses were not selected.
[e] In use, one side of each disk is "depolished"; no other restrictions are placed on the luminous transmissions.

TABLE 3.—*Spectral transmissions, T_λ of glasses selected by AAR Signal Section Committee VI as defining the chromaticity limits of railroad signal colors*

Wavelength in millimicrons	Red						Yellow						Green					
	Pressed ware and disk		Highway crossing		Hand lantern globes		Pressed ware		Disk		Hand lantern globes		Pressed ware		Disk		Hand lantern globes	
	L 154	*D* 86	*L* 75	*D* 400	*L* 201	*D* 211	*L* 141	*D* 142	— 199	— 200	*L* 261	*D* 271	*L* 134	*D* 87	*L* 139	*D* 140	*L* 137	*D* 322
380							0.008	0.0002		0.0008			0.121	0.073	0.097	0.040	0.230	0.13
90							.008	.0002		.0009			.242	.152	.150	.082	.294	.19
400							.0075	.0002		.0010			.335	.237	.207	.126	.356	.247
10							.0074	.0002		.0014			.405	.307	.266	.174	.408	.304
20							.0076	.0003		.0020			.464	.366	.315	.222	.457	.362
30							.0087	.0004		.0028			.521	.425	.371	.273	.505	.416
40							.0113	.0007		.0039			.565	.480	.414	.326	.545	.465
450							.0169	.0014		.0054			.617	.541	.459	.373	.582	.512
60							.0271	.0030		.0075			.659	.588	.503	.423	.620	.552
70							.0423	.0064		.0101			.686	.625	.540	.459	.645	.581
80							.0636	.0126		.0137			.696	.638	.565	.483	.662	.600
90							.0952	.0238		.0190			.695	.633	.577	.501	.666	.600
500							.1324	.0424	0.0000	.0289	0.000		.680	.618	.578	.501	.658	.580
10							.186	.0712	.0001	.0526	.001		.656	.584	.569	.483	.628	.540
20							.241	.1102	.0003	.0826	.120	0.000	.610	.536	.536	.450	.578	.481
30							.303	.158	.0126	.1125	.518	.001	.540	.450	.493	.396	.509	.404
40							.367	.214	.289	.157	.705	.048	.462	.366	.430	.333	.434	.319
550							.430	.277	.654	.277	.767	.433	.382	.279	.358	.266	.347	.234
60							.492	.339	.784	.544	.796	.670	.301	.205	.292	.201	.265	.164
70		0.0000					.542	.399	.826	.770	.818	.738	.230	.1424	.224	.1442	.196	.105
80		.0001	0.0000		0.000		.589	.451	.844	.848	.835	.774	.171	.0952	.172	.0996	.1390	.064
90	0.0000	.0002	.037	0.0000	.001		.625	.495	.857	.873	.848	.803	.1211	.0609	.1240	.0660	.0968	.0372
600	.0003	.0005	.27	.010	.051	0.000	.654	.532	.864	.892	.859	.824	.0856	.0375	.0902	.0428	.0653	.0217
10	.037	.0019	.54	.16	.41	.004	.676	.559	.869	.887	.866	.840	.0588	.0225	.0642	.0276	.0437	.0124
20	.41	.022	.685	.60	.715	.22	.693	.579	.874	.890	.870	.854	.0402	.0134	.0460	.0173	.0289	.0072
30	.71	.23	.742	.796	.805	.60	.705	.593	.879	.892	.873	.863	.0270	.0084	.0322	.0109	.0190	.0041
40	.796	.65	.771	.848	.835	.734	.713	.599	.883	.893	.875	.871	.0182	.0051	.0230	.0070	.0127	.0024
650	.820	.798	.790	.866	.846	.784	.718	.602	.887	.894	.876	.877	.0124	.0031	.0167	.0046	.0088	.0015
60	.833	.833	.804	.873	.853	.803	.721	.603	.889	.894	.877	.880	.0088	.0019	.0122	.0031	.0062	.001
70	.842	.844	.817	.879	.858	.813	.723	.601	.890	.894	.877	.883	.006	.001	.0093	.0021	.0045	.000
80	.848	.852	.826	.881	.860	.820	.723	.596	.891	.894	.876	.884	.004	.000	.0070	.0014	.003	
90	.851	.856	.834	.882	.861	.825	.722	.588	.891	.893	.875	.885	.003		.0054	.001	.0025	
700	.853	.858	.841	.883	.862	.826	.720	.580	.891	.892	.873	.884	.002		.0042	.000	.002	
10	.852	.859	.846	.884	.860	.826	.717	.570	.891	.890	.871	.882	.0015		.0033		.0015	
20	.850	.858	.851	.883	.857	.824	.712	.560	.890	.888	.868	.880	.001		.0026		.001	
30	.848	.857	.854	.881	.855	.821	.706	.548	.889	.886	.865	.879	.000		.0021		.000	
40	.846	.855	.857	.879	.852	.818	.700	.535	.888	.884	.862	.877			.0017			
750	.843	.852	.857	.877	.848	.814	.692	.522	.886	.883	.859	.875			.0014			
60	.840	.849	.857	.875	.844	.809	.683	.507	.884	.882	.856	.873			.0011			
70	.836	.846	.857	.873	.841	.805	.673	.492	.882	.881	.853	.871			.0008			

Wavelength in millimicrons	Blue		Purple		Lunar white	
	L 161	*D* 161	*L* 162	*D* 162	*L* 163	*D* 163
380	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
90	.0000	.0000	.0000	.0000	.0000	.0000
400	.0000	.0000	.0000	.0000	.0000	.0000
10	.0000	.0000	.0000	.0000	.0000	.0000
20	.0000	.0000	.0000	.0000	.0000	.0000
30	.0000	.0000	.0000	.0000	.0000	.0000
40	.0000	.0000	.0000	.0000	.0000	.0000
450	.0000	.0000	.0000	.0000	.0000	.0000
60	.0000	.0000	.0000	.0000	.0000	.0000
70	.0000	.0000	.0000	.0000	.0000	.0000
80	.0000	.0000	.0000	.0000	.0000	.0000
90	.0000	.0000	.0000	.0000	.0000	.0000
500	.0000	.0000	.0000	.0000	.0000	.0000
10	.0000	.0000	.0000	.0000	.0000	.0000
20	.0000	.0000	.0000	.0000	.0000	.0000
30	.0000	.0000	.0000	.0000	.0000	.0000
40	.0000	.0000	.0000	.0000	.0000	.0000
550	.0000	.0000	.0000	.0000	.0000	.0000
60	.0000	.0000	.0000	.0000	.0000	.0000
70	.0000	.0000	.0000	.0000	.0000	.0000
80	.0000	.0000	.0000	.0000	.0000	.0000
90	.0000	.0000	.0000	.0000	.0000	.0000
600	.0000	.0000	.0000	.0000	.0000	.0000
10	.0000	.0000	.0000	.0000	.0000	.0000
20	.0000	.0000	.0000	.0000	.0000	.0000
30	.0000	.0000	.0000	.0000	.0000	.0000
40	.0000	.0000	.0000	.0000	.0000	.0000
650	.0000	.0000	.0000	.0000	.0000	.0000
60	.0000	.0000	.0000	.0000	.0000	.0000
70	.0000	.0000	.0000	.0000	.0000	.0000
80	.0000	.0000	.0000	.0000	.0000	.0000
90	.0000	.0000	.0000	.0000	.0000	.0000
700	.0000	.0000	.0000	.0000	.0000	.0000
10	.0000	.0000	.0000	.0000	.0000	.0000
20	.0000	.0000	.0000	.0000	.0000	.0000	.0000
30	.0000	.0000	.0000	.0000	.0000	.0000	.0000
40	.0000	.0000	.0000	.0000	.0000	.0000	.0000
750	.0000	.0000	.0000	.0000	.0000	.0000	.0000
60	.0000	.0000	.0000	.0000	.0000	.0000	.0000
70	.0000	.0000	.0000	.0000	.0000	.0000	.0000

Wavelength in millimicrons	Blue				Purple				Lunar white			
	Pressed ware		Hand lantern globes		Kerosine		Electric		Kerosine		Electric	
	L 47	D 57	L 141	D 131	L 56	D 47	L 80	D 108	L 45	D 74	L 124	D 73
380	0.579	0.442	0.50	0.45	0.835	0.783	0.886	0.875	0.828	0.835	0.825	0.819
90	.716	.596	.63	.58	.853	.849	.867	.858	.856	.854	.875	.890
400	.770	.675	.710	.655	.857	.852	.838	.827	.873	.867	.888	.900
10	.790	.718	.738	.685	.831	.823	.787	.780	.867	.858	.884	.888
20	.785	.731	.742	.691	.798	.779	.727	.714	.847	.830	.876	.869
30	.771	.726	.734	.680	.763	.733	.647	.625	.838	.820	.871	.860
40	.751	.707	.717	.659	.727	.684	.558	.527	.830	.807	.866	.851
450	.719	.673	.693	.630	.676	.625	.448	.422	.818	.792	.862	.842
60	.670	.625	.652	.576	.615	.552	.328	.302	.800	.769	.851	.826
70	.590	.530	.564	.470	.504	.426	.197	.172	.764	.718	.824	.792
80	.467	.393	.426	.320	.355	.269	.098	.077	.698	.637	.783	.733
90	.331	.258	.286	.186	.214	.1397	.0408	.0304	.612	.535	.732	.656
500	.225	.168	.197	.112	.1305	.0713	.0189	.0130	.542	.446	.672	.583
10	.1362	.0854	.117	.0529	.0636	.0275	.0076	.0045	.450	.350	.598	.495
20	.0710	.0376	.0601	.0215	.0266	.0087	.0032	.0017	.357	.258	.520	.408
30	.0319	.0135	.0270	.0075	.0088	.0022	.0016	.0007	.266	.174	.434	.319
40	.0191	.0072	.0188	.0044	.0050	.0010	.0017	.0008	.230	.143	.397	.281
550	.0219	.0084	.0244	.0067	.0073	.0017	.0039	.0019	.255	.164	.423	.307
60	.0325	.0123	.0361	.0109	.0147	.0042	.0056	.0029	.306	.211	.470	.357
70	.0254	.0083	.0280	.0071	.0119	.0031	.0023	.0011	.291	.195	.462	.342
80	.0092	.0022	.0096	.0016	.0033	.0006	.0004	.0002	.203	.1231	.373	.253
90	.0024	.0004	.0026	.0003	.0006	.0001	.0001	.0000	.132	.0675	.282	.173
600	.0020	.0003	.0021	.0002	.0005	.0001	.0001	.0000	.128	.0651	.277	.170
10	.0022	.0005	.0021	.0002	.0007	.0001	.0001	.0001	.141	.0743	.293	.185
20	.0019	.0002	.0023	.0003	.0008	.0001	.0001	.0001	.145	.0778	.299	.190
30	.0015	.0002	.0021	.0002	.0007	.0001	.0001	.0001	.138	.0740	.292	.183
40	.0010	.0001	.0016	.0001	.0005	.0001	.0001	.0000	.128	.0654	.276	.168
650	.0010	.0001	.0015	.0001	.0006	.0001	.0001	.0000	.131	.0688	.283	.174
60	.0015	.0002	.0020	.0002	.0018	.0003	.0002	.0001	.165	.0942	.327	.214
70	.0035	.0003	.0054	.0006	.0075	.0015	.0012	.0004	.248	.161	.425	.302
80	.0109	.0005	.017	.0052	.043	.016	.0080	.0045	.398	.303	.560	.453
90	.0275	.0020	.042	.014	.19	.11	.045	.036	.587	.514	.707	.628
700	.042	.0030	.071	.027	.44	.35	.18	.16	.734	.700	.810	.766
10	.050	.0040	.090	.037	.68	.61	.41	.38	.821	.812	.865	.846
20	.051	.0041	.096	.041	.80	.77	.62	.60	.854	.862	.888	.880
30	.049	.0037	.096	.040	.859	.84	.76	.75	.872	.884	.900	.892
40	.047	.0034	.093	.039	.882	.874	.84	.83	.877	.893	.902	.897
750	.045	.0031	.090	.037	.892	.885	.878	.875	.878	.895	.903	.899
60	.043	.0026	.087	.035	.895	.889	.897	.895	.878	.895	.904	.900
70	.041	.0021	.084	.033	.896	.890	.902	.902	.878	.895	.904	.900
T_{AAR}=	130.2	74.7	124.8	56.0	131.2	73.3	40.1	30.3	121.7	79.6	205.3	146.6

TABLE 4.—*Luminous transmissions, T_w, ratios of red to total luminous transmission, T_r/T_w, and chromaticity coordinates, x, y, z, for glasses selected by AAR Signal Section Committee VI as defining the chromaticity limits of railroad signal colors*

Color designation	Number of glass	Illuminant at 1,900° K				Illuminant at 2,360° K						Illuminant at 2,848° K			
		x	y	z	T_w	x	y	z	T_w	T_{AAR}	T_r/T_w	x	y	z	T_w
Red	154	0.7148	0.2852	0.0000	0.1564	0.7138	0.2862	0.0000	0.1222	177.0	----------	0.7132	0.2867	0.0000	0.1009
	86	.7234	.2766	.0000	.0944	.7228	.2772	.0000	.0711	102.9	----------	.7224	.2776	.0000	.0572
	75	.6967	.3032	.0001	.2431	.6944	.3055	.0001	.1989	288.2	----------	.6927	.3072	.0001	.1698
	400	.7108	.2891	.0001	.1898	.7096	.2904	.0001	.1502	217.6	----------	.7088	.2912	.0001	.1251
	201	.7051	.2948	.0001	.2205	.7036	.2963	.0001	.1771	256.7	----------	.7025	.2974	.0001	.1493
	211	.7178	.2822	.0000	.1300	.7171	.2829	.0000	.1004	145.5	----------	.7165	.2835	.0000	.0823
Yellow	141	.5063	.3976	.0062	.5571	.5740	.4157	.0103	.5296	214.1	----------	.5560	.4291	.0149	.5082
	142	.6113	.3861	.0027	.4262	.5934	.4026	.0041	.3978	160.8	----------	.5794	.4151	.0056	.3762
	199	.6036	.3955	.0009	.7137	.5878	.4111	.0011	.6692	270.5	----------	.5762	.4226	.0012	.6334
	200	.6147	.3836	.0018	.6708	.6000	.3972	.0027	.6210	251.0	----------	.5889	.4073	.0038	.5823
	261	.5873	.4107	.0020	.7669	.5669	.4306	.0026	.7358	297.4	----------	.5515	.4454	.0030	.7095
	271	.6151	.3843	.0007	.6456	.6014	.3979	.0008	.5967	241.2	----------	.5913	.4078	.0009	.5584
Green	134	.3197	.4944	.1859	.2106	.2749	.4550	.2702	.2442	205.9	----------	.2448	.4145	.3407	.2098
	87	.2684	.4976	.2340	.1492	.2316	.4472	.3212	.1784	150.5	----------	.2084	.4016	.3899	.2013
	139	.3407	.5025	.1568	.2002	.2951	.4721	.2328	.2294	193.4	----------	.2634	.4376	.2990	.2515
	140	.2949	.5138	.1913	.1397	.2555	.4742	.2702	.1645	138.7	----------	.2295	.4348	.3357	.1835
	137	.3025	.4974	.2001	.1872	.2602	.4542	.2856	.2193	184.9	----------	.2324	.4116	.3561	.2440
	322	.2415	.4942	.2643	.1236	.2099	.4376	.3525	.1502	126.6	----------	.1909	.3891	.4200	.1712
Blue	47	.1783	.2049	.6168	.02216	.1595	.1521	.6884	.02909	130.2	0.0089	.1530	.1221	.7249	.03556
	57	.1458	.1387	.7154	.01164	.1436	.1051	.7514	.01669	74.7	.0011	.1440	.0862	.7698	.02155
	141	.1916	.2070	.6014	.02173	.1665	.1522	.6812	.02789	124.8	.0147	.1575	.1212	.7213	.03372
	131	.1543	.1187	.7270	.00876	.1482	.0889	.7630	.01252	56.0	.0088	.1474	.0728	.7798	.01626
Purple	56	.2280	.1475	.6245	.01386	.1765	.1035	.7200	.01692	131.2	.116	.1610	.0818	.7572	.02062
	47	.2158	.1000	.6842	.00752	.1700	.0690	.7610	.00945	73.3	.158	.1579	.0552	.7869	.01200
	80	.2292	.0904	.6804	.00443	.1799	.0564	.7636	.00517	40.1	.188	.1661	.0426	.7913	.00634
	108	.2277	.0758	.6965	.00336	.1786	.0463	.7750	.00390	30.3	.227	.1658	.0352	.7990	.00485
Lunar white	45	.4395	.3981	.1624	.2173	.3651	.3664	.2685	.2306	121.7	----------	.3122	.3279	.3599	.2421
	74	.4005	.3766	.2229	.1394	.3216	.3308	.3476	.1509	79.6	----------	.2711	.2852	.4437	.1612
	124	.4822	.4106	.1072	.3755	.4169	.3953	.1878	.3891	205.3	----------	.3654	.3688	.2658	.4004
	73	.4556	.4032	.1413	.2643	.3840	.3772	.2388	.2779	146.6	----------	.3308	.3426	.3266	.2895

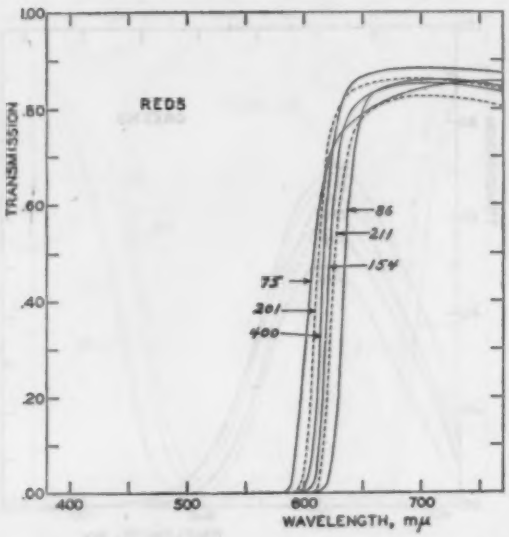

FIGURE 1.—*Spectral transmissions of standard limit glasses designated as red.*
Glasses 154 and 86, pressed ware and disk; 75 and 400, highway crossing; 201 and 211, lantern. See tables 2 and 3 for further identification.

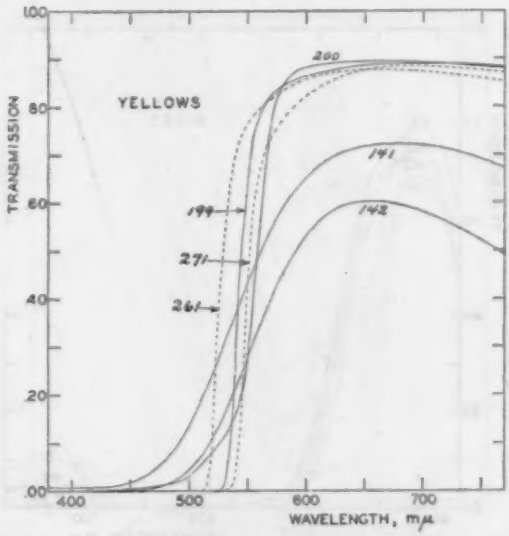

FIGURE 2.—*Spectral transmissions of standard limit glasses designated as yellow.*
Glasses 141 and 142, pressed ware (non-HR); 199 and 200, disk; 261 and 271, lantern. See tables 2 and 3 for further identification.

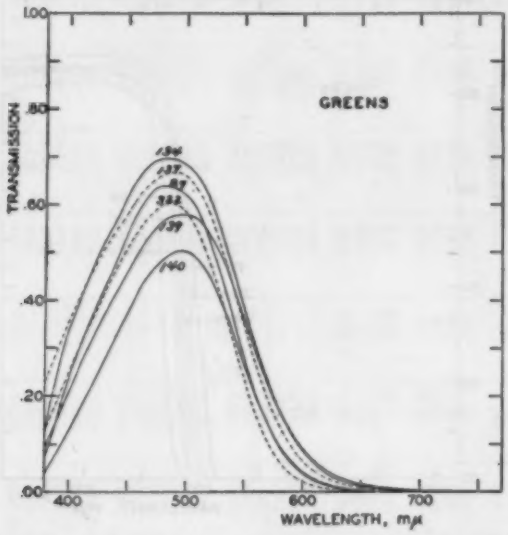

FIGURE 3.—*Spectral transmissions of standard limit glasses designated as green.*
Glasses 134 and 87, pressed ware (non-HR), 139 and 140, disk; 137 and 322, lantern. See tables 2 and 3 for further identification.

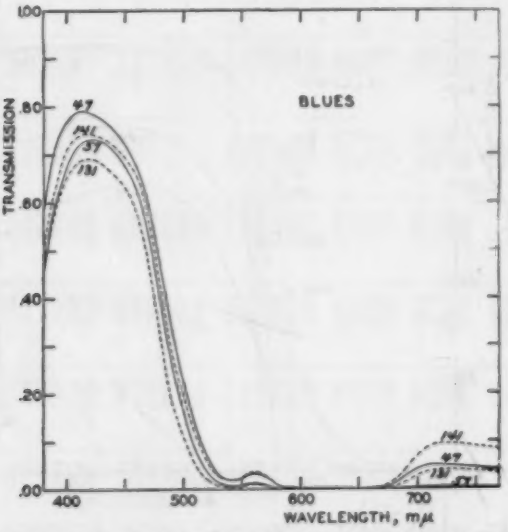

FIGURE 4.—*Spectral transmissions of standard limit glasses designated as blue.*
Glasses 47 and 57, pressed ware; 141 and 131, lantern. See tables 2 and 3 for further identification.

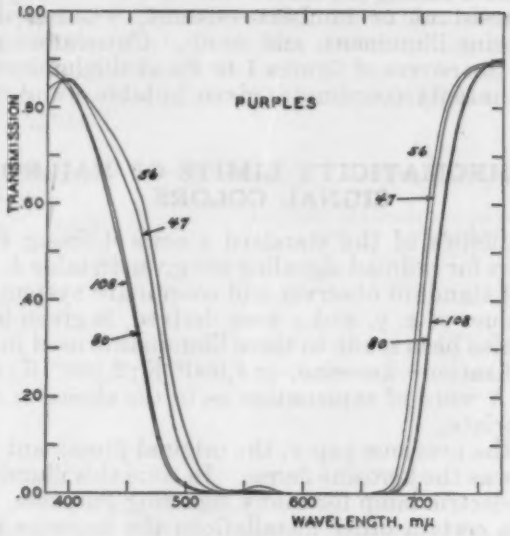

FIGURE 5.—*Spectral transmissions of standard limit glasses designated as purple.*
Glasses 56 and 47, kerosine; 80 and 108, electric. See tables 2 and 3 for further identification.

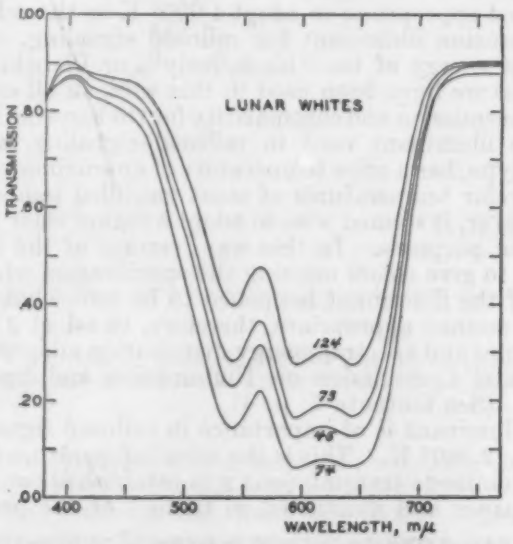

FIGURE 6.—*Spectral transmissions of standard limit glasses designated as lunar white.*
Glasses 45 and 74, kerosine; 124 and 73, electric. See tables 2 and 3 for further identification.

Other differences among the curves correlate with the type of glass—whether heat-resistant or nonheat-resistant, whether designed for electric or kerosine illuminant, and so on. Correlation may also be noted between the curves of figures 1 to 6 and the luminous transmissions and chromaticity coordinates given in table 4 and illustrated in figures 8 and 9.

IV. CHROMATICITY LIMITS OF RAILROAD SIGNAL COLORS

The chromaticities of the standard glasses defining the limits of acceptable colors for railroad signaling are given in table 4. Reference to the 1931 ICI standard observer and coordinate system, in terms of which these values of x, y, and z were derived, is given in section II. Reference has also been made to three illuminants used in the railroad signal standardization—kerosine, or 1,900° K; 2,360° K; and electric, or 2,848° K. A word of explanation as to the choice of these illuminants is appropriate.

As noted in the previous paper, the original illuminant used in railroad signaling was the kerosine flame. In time this illuminant was replaced by the electric lamp for many signaling purposes, but in hand lanterns and in certain other installations the kerosine flame is still used. In some cases the same type of glass can be used and will give an acceptable signal with either illuminant; in others, different types have to be used for each illuminant.

The color temperature of the kerosine flame varies with the type of burner. That of the signal burners is close to 1,900° K. It therefore seemed appropriate to adopt 1,900° K as the color temperature of the kerosine illuminant for railroad signaling, and spectral distributions of energy of the "black body", or Planckian radiator, at this temperature have been used in this work in all computations of luminous transmission and chromaticity for the kerosine illuminant.[15]

The electric illuminant used in railroad signaling, at least one very common type, has a color temperature of approximately 2,680° K. As the rated color temperatures of most gas-filled lamps are higher than this, however, it seemed wise to adopt a higher color temperature for specification purposes. In this way, certain of the limit glasses would not fail to give colors meeting the specification when the color temperature of the illuminant happened to be somewhat higher than 2,680° K. It seemed appropriate, therefore, to select 2,848° K, the color temperature and spectral-energy distribution adopted in 1931 by the International Commission on Illumination and known as ICI illuminant A. (See footnote 7, p. 4).

One other illuminant is of importance in railroad signal standardization, namely, 2,360° K. This is the color temperature at which the T_{AAR} scale of luminous transmissions was established, as explained in the previous paper and illustrated in table 1 of the present paper.

[15] As is well known, the exact values of radiant energy for any specified temperature depend on the value of C_2 in Planck's equation

$$E_\lambda = \frac{C_1 \lambda^{-5}}{e^{\frac{C_2}{\lambda\theta}} - 1}.$$

For continuity with the published reports and specifications, the value of $C_2 = 14{,}350$ micron-degrees is retained. Recent values have varied from 14,320 on the International Temperature Scale to 14,360, as recommended by Wensel, J. Research NBS 22, 375 (1939) RP1189. All values of color temperature in this paper are based on $C_2 = 14{,}350$.

This color temperature is of little importance to the chromaticity specifications, being intermediate to the other two; but values of x, y, and z are given to indicate the course of the chromaticity loci for the respective glasses as the color temperature of the illuminant is varied over the range from 1,900 to 2,848° K. These loci are illustrated in figure 7.

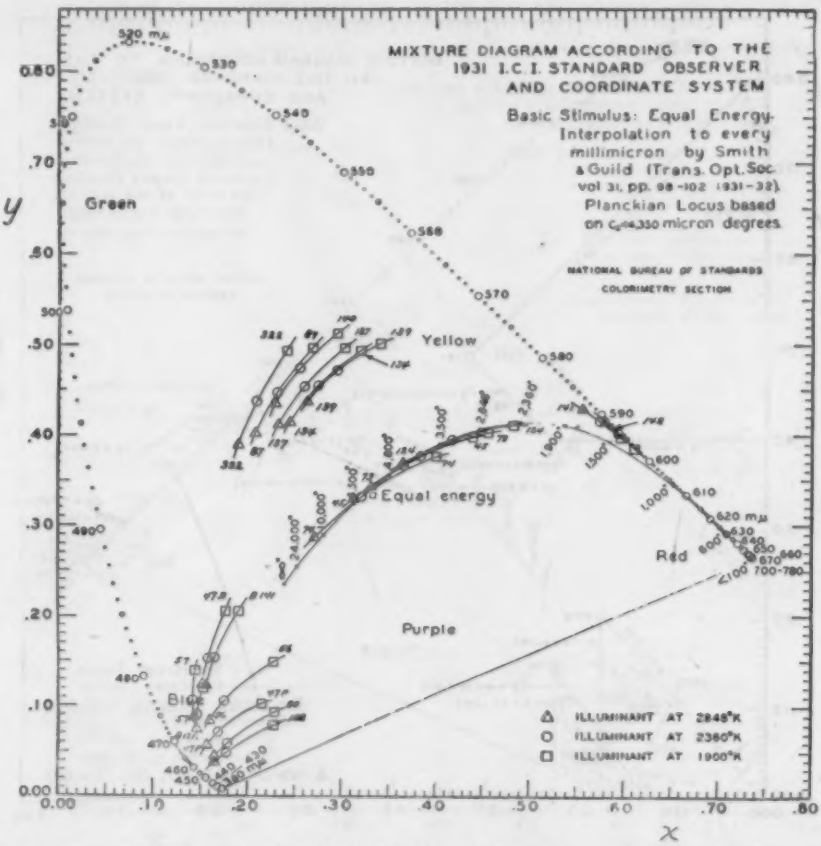

FIGURE 7.—*ICI chromaticity (mixture) diagram showing variations in the chromaticity (x, y) of signal glasses as the illuminant is changed from 1,900° through 2,360° to 2,848° K.*

It is apparent that in defining areas of acceptable chromaticity on the chromaticity diagram, one is interested primarily in the particular illuminant-glass combinations used in actual signaling practice. For example, certain of the glasses are designed for use only with kerosine illuminant and certain others for use only with electric illuminants; see table 2. Others like the nonheat-resisting (non-HR) yellows and certain greens are used with both illuminants. A specification for signal colors (illuminant-glass combinations) must take this into account.

The areas finally selected and in current status are shown in figure 8, which is a reproduction of the diagram illustrating part A of AAR Signal Section specification 69–40 for signal colors, excluding kerosine hand lantern globes, and in figure 9, which is a reproduction of the corresponding diagram in specification 59–39 for kerosine hand lantern globes. Large-scale sections of parts of figure 8 are shown also in figures 10 to 12.

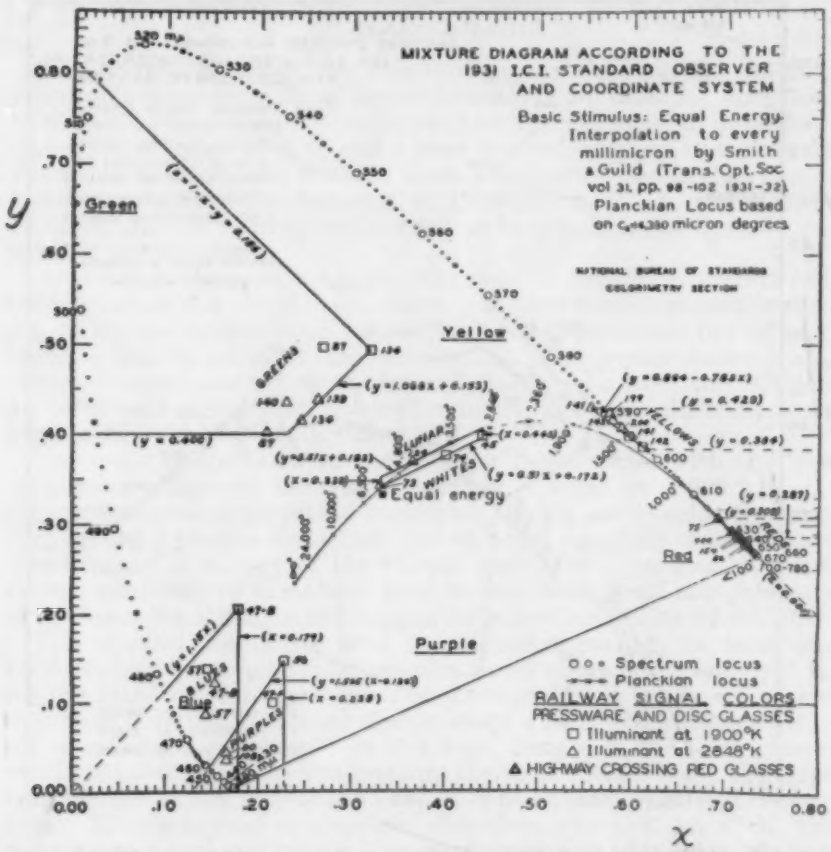

FIGURE 8.—*ICI chromaticity (mixture) diagram showing the permissible areas for railroad signal colors and the locations of the standard limit glasses for the designated illuminants, according to AAR Signal Section specification 69–40.*

In figures 8 and 9 [16] may be noted (1) the spectrum locus from 380 to 780 mμ, (2) the Planckian locus from <100° K to ∞° K, (3) the equations defining the straight lines bounding the areas of permissible chromaticities, and (4) the point for each standard glass plotted for illuminant at 1,900° and/or 2,848° K.

A chart similar to figure 8 has appeared in the various AAR Signal Section specifications, beginning in 1935, these being based on recom-

[16] In figures 8, 9, and 13, certain of the numbers designating the blue and purple glasses carry the auxiliary designations *B* or *P*, as engraved on the glasses. In the rest of the paper, however, these letters have been omitted as they seemed unnecessary and somewhat confusing.

mendations made to the signal engineers in 1933, as already noted. The chart shown in figure 9 first appeared in 1938 in specification 59–38. The areas from specification 69–38 were incorporated so far as possible into 59–38, deviations being made only where the standard glasses selected for 59–38 would not fall within the areas already selected for 69–38.

Some discussion should be given regarding the reasons leading to the choice of boundary lines in figure 8. Obviously, simplicity of

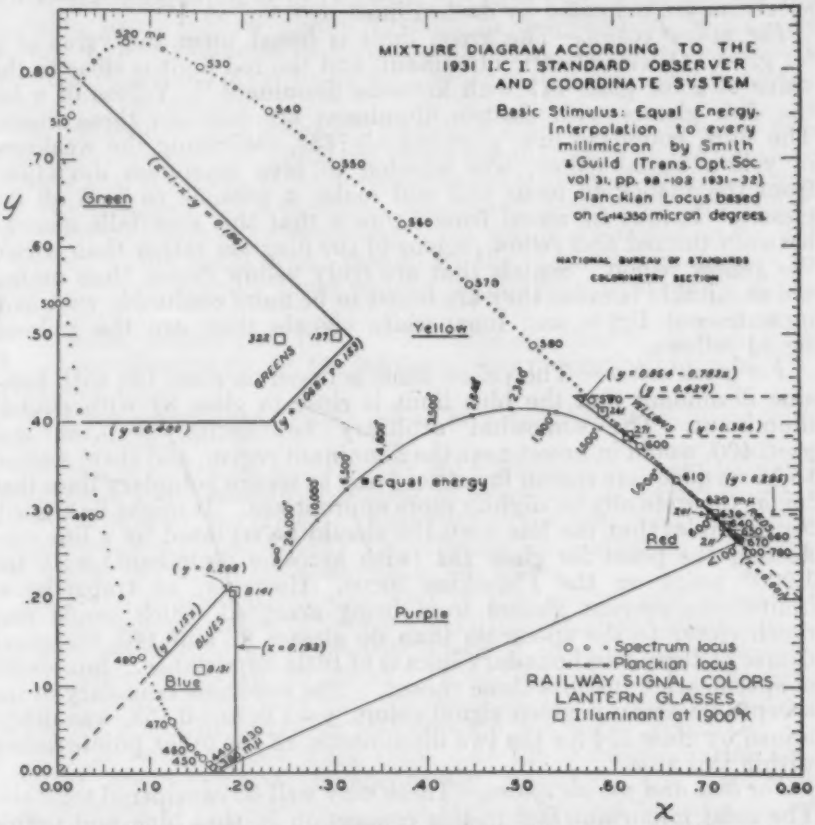

FIGURE 9.—*ICI chromaticity (mixture) diagram showing the permissible areas for hand lantern colors and the locations of the standard limit glasses for 1,900° K illuminant, according to AAR Signal Section specification 59–39.*

specification will be secured by using lines parallel to the x or y axes, at 45° to these axes, or passing through the origin. Where possible, then, such boundaries were used; deviations from such boundaries were made only when it seemed desirable for special reasons. These boundaries of figure 8 and specification 69–40 are considered in detail in the following sections.

For red colors.—The area is defined by the lines $y=0.308$ (for highway-crossing red) or 0.287 (for other reds) and $z=0.001$. Reference to table 4 shows that these values of y represent closely the yellow limits for the respective reds as given by the respective standard

limit glasses when used with electric illuminant. Kerosine illuminant gives lesser values of y for the same glasses, which is satisfactory. The z limit is a rather liberal tolerance for selenium red glasses, but there is no need to make it more restrictive. Here, as with most of the other colors, the spectrum automatically forms one boundary of the permissible area, but this spectrum line does not need to be specified. It may be noted that the parts of the areas enclosed by the spectrum and the line joining the red and violet ends of the spectrum are indicated by continuous lines. The extensions of these lines beyond the spectrum are indicated by dashed lines.

For yellow colors.—The green limit is based upon the value of y for glass 141 with electric illuminant, and the red limit is close to the value of y for glass 142 with kerosine illuminant.[17] Values of y for the disk glasses with electric illuminant are between these limits. The third boundary line, $y=0.864-0.783x$, restricting the weakness of yellow signal colors, was selected to give maximum deviations from the Planckian locus and still make it possible to pass all the glasses. It may be noted from figure 8 that this area falls midway between the red and yellow regions of the diagram rather than within the yellow region. Signals that are truly yellow rather than orange are unsuitable because they are found to be more confusible with bare incandescent lights and lunar-white signals than are the railroad signal yellows.

For green colors.—The yellow limit is based on glass 134 with kerosine illuminant and the blue limit is close to glass 87 with electric illuminant. The somewhat arbitrary boundaries, $z=0.186$ and $y=0.400$, would intersect near the illuminant region, and there seemed to be no adequate reason for attempting to secure boundary lines that might theoretically be slightly more appropriate. It might be argued, for example, that the line $z=0.186$ should be replaced by a line connecting the point for glass 134 (with kerosine illuminant) with the 1,900° point on the Planckian locus. However, as transmission limitations prevent glasses from being accepted which would plot much closer to the spectrum than do glasses 87 and 140, the exact course of these two boundary lines is of little importance. Simplicity of specification justifies those chosen. The weakness boundary of the acceptable area for green signal colors, $y=1.068x+0.153$, was determined by glass 134 for the two illuminants, all the other points falling within this area.

For blue and purple colors.—These may well be considered together. The most important fact in this connection is, that blue and purple signals are not differentiated by the engineer by their chromaticities in the usual sense. Note in figure 8 that the "purple" signals do not fall in the purple region of the diagram. The blue must not be mistaken for green or lunar white or for the dichromatic purple; the purple must be recognized as a dichromatic (red-blue) signal.[18] It therefore seemed adequate to use the simple triangular areas shown, the overlapping being of no consequence.

For lunar-white colors.—These must be differentiated from yellow, green, and blue. The yellow boundary is based on glass 45 with

[17] This boundary was originally at $y=0.386$, given by glass 142 with kerosine illuminant, but was later lowered to $y=0.384$ to include the red limit of lantern yellow, No. 271.

[18] Because of chromatic aberration of the lens system of the human eye, the dichromatic image is normally a red center with a blue halo or surround, though this will vary with the vision of the observer. Neither blue nor purple are used as long-range high-speed signals.]

kerosine illuminant, the blue boundary on glass 73 with electric illuminant. Green and purple limits, as such, were not selected.[19] It was believed that manufacturing tolerances were well represented by the glasses selected. Accordingly, the rhomboidal area shown in figure 8 was specified. An equally satisfactory specification can be prepared in terms of deviations from the Planckian locus combined with blue and yellow limits; this has been done with aviation colors.[20]

The signals using kerosine illuminant and covered in specification 69–40 are differentiated in railroad purchase specifications from the kerosine hand lantern globes covered in specification 59–39. As already noted, the areas of specification 59–39, figure 9, were made identical with those of 69–40, figure 8, so far as possible. The following points may be noted.

For red lantern-globe colors.—The yellow limit is given by $y=0.295$. The color perception of signal red varies toward yellow as the intensity of the signal is increased. Lantern reds are low-intensity signals, and a yellower signal was accordingly considered permissible. (The yellow limit of highway-crossing red, $y=0.308$, is permitted to be still yellower. This signal is not viewed by the engineer and there is no yellow, except possibly those of bare illuminants, with which it can be confused.)

For yellow lantern-globe colors.—The area specified is identical with that in specification 69–40, the red limit being determined by glass 271, as already noted.

For green lantern-globe colors.—The area specified is identical with that in specification 69–40.

For blue lantern-globe colors.—The red transmission cannot be eliminated from heat-resisting blue glass as effectively as from the other kind of blue glass, see table 3. Accordingly, the x-boundary had to be moved from 0.179 to 0.192, necessitating an additional boundary ($y=0.208$) to restrict the weakness of the colors.

Based on considerations discussed in this section and consistent with the diagrams shown in figures 8 and 9, specifications of chromaticity were established and included in part A of AAR Signal Section Specification 69–40 and of 59–39. In addition to the chromaticity limits specified in part A of each specification, there are given also the minimum limits of luminous transmission for signal glassware, expressed in terms of the T_{AAR} scale. As the intensities of the illuminants are otherwise independently specified, the luminous transmissions of the glassware serve as an adequate specification of the intensities of the signal colors. The following quotations are taken from these specifications:

From AAR Signal Section Specification 69–40, Part A:

5. Red.—(a) Three types of red ware are used: (1) pressed ware, for which the value of T_{AAR} shall be not less than 85, (2) thin polished discs, for which the value of T_{AAR} shall be not less than 115, and (3) highway crossing roundels, for which the value of T_{AAR} shall be not less than 220; in cases (1) and (2) the value of y shall be not greater than 0.287, and in case (3) not greater than 0.308, and in all three cases the value of z shall be not greater than 0.001.

6. Yellow.—(a) Two types of yellow glass are used: (1) the non-heat-resisting type, for which the value of T_{AAR} shall be not less than 130, and (2)

[19] Lunar-white glasses are "cobalt blue" glasses. Experience indicates that important deviations in the green or purple directions do not occur in the manufacture of such glasses.

[20] Army-Navy Aeronautical Specification: Colors; Aeronautical lights and lighting equipment; AN–C–56 (1942).

the heat-resisting type, designed for use in thin discs with electric illuminant, which must have one surface depolished and for which the value of T_{AAR} need not be specified; in both cases the value of y shall be not greater than 0.429 nor less than 0.384, also not less than $0.864-0.783x$.

7. Green.—(a) Two types of green glass are used: (1) the non-heat-resisting type, for which the value of T_{AAR} shall be not less than 150, and (2) the heat-resisting type, designed for use in thin polished discs with electric illuminant, for which type the value of T_{AAR} shall be not less than 138; in both cases the value of y shall be not less than 0.400 nor less than $1.068x+0.153$, and the value of z not less than 0.186.

8. Blue.—(a) The value of T_{AAR} shall be not less than 75; the value of x shall be not greater than 0.179, and the value of y not greater than $1.15x$; the value of T_r/T_w shall be not greater than 0.008.

9. Purple.—(a) Two types of purple glass are used: (1) that designed for use with kerosene illuminant, for which type the value of T_{AAR} shall be not less than 73 and the value of T_r/T_w not less than 0.116, and (2) that designed for use with electric illuminant, for which type the value of T_{AAR} shall be not less than 30 and the value of T_r/T_w not less than 0.187; in both cases the value of x shall be not greater than 0.228, and the value of y not greater than $1.505(x-0.130)$, nor shall the value of T_r/T_w be greater than 0.240.

10. Lunar White.—(a) Two types of lunar white glass are used: (1) that designed for use with kerosene illuminant, for which type the value of T_{AAR} shall be not less than 80, and (2) that designed for use with electric illuminant, for which type the value of T_{AAR} shall be not less than 147; in both cases the value of x shall be not greater than 0.440 nor less than 0.330 and the value of y not greater than $0.51x+0.183$ nor less than $0.51x+0.172$.

From AAR Signal Section Specification 59–39, Part A:

5. Red.—(a) The value of T_{AAR} shall be not less than 140; the value of y shall be not greater than 0.295; and the value of z not greater than 0.001.

6. Yellow.—(a) The value of T_{AAR} shall be not less than 200; the value of y shall be not greater than 0.429 nor less than 0.384, also not less than $0.864-0.783x$.

7. Green.—(a) The value of T_{AAR} shall be not less than 125; the value of y shall be not less than 0.400 nor less than $1.068x+0.153$, and the value of z not less than 0.186.

8. Blue.—(a) The value of T_{AAR} shall be not less than 55; the value of x shall be not greater than 0.192 and the value of y not greater than 0.208 nor greater than $1.15x$; the value of T_r/T_w shall be not greater than 0.015.

V. TOLERANCES FOR CERTIFYING DUPLICATES OF STANDARD LIMIT GLASSES

Part A of specification 69–40 and of 59–39 serve as a fundamental specification of the colors (chromaticities and intensities) of railroad signals. As such they are adequate for use by any standardizing laboratory equipped to make accurate spectrophotometric measurements or otherwise to derive accurate colorimetric data based on the 1931 ICI standard observer and coordinate system.

They are not adequate and suitable, however, for use by most glass-manufacturing plants or by inspectors of signal glassware. For such purposes it is apparent that duplicates of the standard limit glasses must be available to the manufacturer or the inspector, so that by simple colorimetric and photometric comparisons it can quickly be determined whether any glassware in question comes within the tolerances given in part A of each specification.

In a continuation, therefore, of the work already undertaken by the three cooperating agencies, it was agreed that Corning Glass Works should prepare duplicates of the standard limit glasses that would be measured by the National Bureau of Standards and, if found satisfactory, certified and issued to those in need of such glasses.

One of the most important questions to be decided in this connection was the magnitude of the tolerances to be adopted in accepting and certifying duplicates of the standard limit glasses. If too liberal tolerances were adopted, one manufacturer might be at a disadvantage relative to another by having a smaller total range within which he must keep his product. If the tolerances were too small, the difficulties of securing a sufficient number of acceptable duplicates would unduly prolong the work, and the time at which the specifications could be promulgated and the duplicates issued would be seriously delayed

The matter was actually decided largely on the basis that the smallest tolerances would be established and used, which would still permit Corning Glass Works to prepare a suitable number of duplicates within reasonable time and cost. This was effective and practical, even if not ideally scientific.

Space does not permit a detailed description of apparatus and procedures used in examining or measuring the hundreds of duplicate glasses submitted. Many of these details may be found in NBS Reports 6 and 7, to which reference has already been made. The following points may be briefly noted:

1. Colorimetric comparisons were made and relative values of luminous transmission were determined mostly by means of a Schmidt & Haensch Martens photometer with a simple two-part 6° photometric field. Most of the work was done with a color temperature of 2,360°K. This was necessary in the determination of T_{AAR} and T_r/T_w, and the field brightnesses were such that it was preferable to work at this color temperature for the chromaticity examinations. Care was taken to ascertain that all duplicates accepted would be valid for illuminants at 1,900° or 2,848°K, consistent with the tolerances to be given in the specifications. Duplicates and standards were so nearly identical that important questions of heterochromatic photometry did not arise.

2. Various methods were used to determine accurately the small chromaticity differences involved.

(a) With the selenium red glasses, where melt number has little significance, a large number of duplicates for each standard were examined and a sample found having a chromaticity differing from the standard by about the amount finally adopted in the specification, the magnitude of this tolerance being always sufficient to include the desired number of acceptable duplicates. The differences in x or y of this tolerance-limit sample from the standard were determined spectrophotometrically.

(*b*) In certain cases—for example, with some of the blues and purples—duplicates of the standard were prepared from the same melt or piece. In such cases no deviations of chromaticity from the standard could be detected, experience indicating that the duplicates were all well within the tolerances finally adopted.

(c) In some cases Lovibond glasses of low number could be inserted in series with the standard until the duplicate was matched in chromaticity. Computation then gave the differences in x or y from the standard. By interpolation, all chromaticities within the tolerance could be measured by means of the Lovibond glasses.

(d) The chromaticities of the diffusing ("depolished") disk-yellow duplicate glasses were determined relative to the polished nondiffusing

standards on a color-temperature comparator having a large Lummer-Brodhun trapezoidal field, with special filters and diffusing plates. Chromaticity matches were made by varying the color temperature of one of the standard lamps.

3. Values of T_r/T_v for the blue and purple glasses were derived from measurements made on the Martens photometer with illuminant at 2,360°K and with a dark-limit red glass (duplicate of 86) over the ocular. This in effect limits the determinations to the visual range 650 to 770 mμ, as called for in the specifications. As with measurements of T_{AAR}, values were determined relative to a closely similar standard, whose value of T_r/T_v had been determined spectrophotometrically.

4. The uniformity of the values of T_{AAR} over the surface of each 2-inch-square duplicate glass was determined by measurements made at four different regions relative to that at the center. Practically all

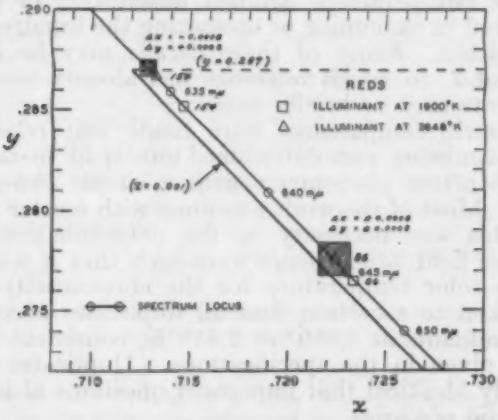

FIGURE 10.—*Large-scale section of figure 8 showing (dark areas) the tolerances in x and y permitted in glasses certified as duplicates of standard limit glasses designated as red, for pressed ware and disks.*

glasses but the selenium reds and yellows were found to be uniform in transmission, that is, the values did not differ from those at the center by as much as 1 percent of the value. All the red glasses, and the disk-yellow and lantern-yellow glasses, are "selenium" glasses, whose color varies with heat treatment. On this account they are usually nonuniform in transmission and chromaticity. This was not tested for the 1-inch-diameter disk-yellow duplicate glasses. For the 2-inch squares prepared as duplicates for lantern yellows and for all the reds, however, the uniformity of luminous transmission was measured. Satisfactory chromaticity duplicates were too rare to permit any rejections for nonuniformity. Instead, the variations of T_{AAR} are given in the certificate, with a note that such variations are usually accompanied by chromaticity variations—the higher the transmission the yellower (or greener) the glass. These variations of transmission often were several percent of the value at the center. Tolerances of Δx and Δy, as finally adopted and given in part B of AAR Signal Glass Specifications 69–40 and of 59–39, are given in table 5. The tolerances for reds 154 and 86, for yellows 141 and 142

and yellows 199 and 200, and for greens 134 and 87 and greens 139 and 140, are illustrated in the large-scale sections of the chromaticity diagram shown in figures 10 to 12. Corresponding diagrams for the other glasses and colors can be plotted from the data of tables 4 and 5 if desired.

TABLE 5.—*Maximum chromaticity deviations permitted for glasses certified as duplicates of standard limit glasses for railroad signaling, AAR Signal Section Specifications 69–40 and 59–39*

Color designation	Number of glass	Color temperature of illuminant	*Chromaticity coordinates, x, y, z,* and maximum deviations, Δx, Δy, Δz, for glasses and illuminants indicated					
			x	Δx	y	Δy	z	Δz
		°K						
Red	154	2848	0.7132	−0.0008	0.2867	+0.0008	0.0000	0.001*
	86	2848	.7224	±.0008	.2776	±.0008	.0000	.001*
	75	2848	.6927	+.0008	.3072	−.0008	.0001	.001*
	400	2848	.7068	±.0008	.2912	±.0008	.0001	.001*
	201	1900	.7051	+.0008	.2948	−.0008	.0001	.001*
	211	1900	.7178	±.0008	.2822	+.0008	.0000	.001*
Yellow	141	2848	.5560	+.0010	.4291	−.0010	.0149	----
	142	2848	.5794	−.0010	.4151	+.0010	.0056	----
	199	2848	.5762	+.0010	.4226	----	.0012	±.0012
	200	2848	.5889	−.0010	.4073	----	.0038	−.0038
	261	1900	.5873	+.0010	.4107	−.0010	.0020	----
	271	1900	.6151	−.0010	.3843	+.0010	.0006	----
Green	134	2848	.2448	−.0015	.4145	−.0015	.3407	----
	87	2848	.2084	±.0015	.4016	±.0015	.3899	----
	139	2848	.2634	−.0015	.4376	−.0015	.2990	----
	140	2848	.2295	±.0015	.4348	±.0015	.3357	----
	137	1900	.3025	−.0015	.4974	−.0015	.2001	----
	322	1900	.2415	±.0015	.4942	±.0015	.2643	----
Blue	47	1900	.1783	−.0020	.2049	−.0020	.6168	----
	57	1900	.1458	+.0020	.1387	+.0020	.7154	----
	141	1900	.1916	−.0030	.2070	{+.0010 −.0020}	.6014	----
	131	1900	.1543	±.0015	.1187	±.0015	.7270	----
Purple	56	1900	.2280	−.0020	.1475	−.0020	.6245	----
	47	1900	.2158	+.0020	.1000	+.0020	.6842	----
	80	2848	.1661	±.0005	.0426	−.0010	.7913	----
	108	2848	.1658	±.0005	.0352	+.0010	.7990	----
Lunar white	45	1900	.4395	−.0015	.3981	±.0010	.1624	----
	74	1900	.4005	−.0020	.3766	+.0020	.2229	----
	124	2848	.3654	±.0010	.3688	±.0010	.2658	----
	73	2848	.3308	±.0010	.3426	+.0020	.3266	----

* This tolerance is given in part A of the signal glass specifications. In effect it limits the tolerances of ±0.0008 in x and y for the dark-limit glasses, as shown in figure 10.

All limit glasses must conform to the restrictions imposed by part A of each specification. This is noted in table 5 for the red glasses by giving the tolerance $\Delta z=0.001$; see also figure 10. Other similar restrictions may be noted for yellow 141, figure 11; green 134, figure 12; and for others.

Probably in most cases the tolerances shown in table 5 are logical in terms of the coordinates used. Where a standard glass is a chromaticity limit it is logical that duplicates of this glass be allowed to deviate toward but not away from the optimum chromaticity. For example, with yellow glass 141, which is a pale and green limit, the restrictions of table 5 (combined with part A) insure that duplicates of this glass can deviate only in the red and more saturated directions.

In other cases the logic of the situation is violated. This is true for red 154. The logical tolerances are $\Delta x=+0.0008$, $\Delta y=-0.0008$, as

are given for reds 75 and 201. With red 154, however, practically all the close duplicate glasses available were in the region $x=0.7132 -0.0008$ and $y=0.2867+0.0008$. To expedite the work, therefore, the tolerances shown were adopted, it being considered that a value of $y=0.2875$ did not exceed the value of $y=0.287$ given in part A of the specification.

Corresponding "reasoning," based on expediency rather than idealism, resulted in some of the other tolerances shown. However, the

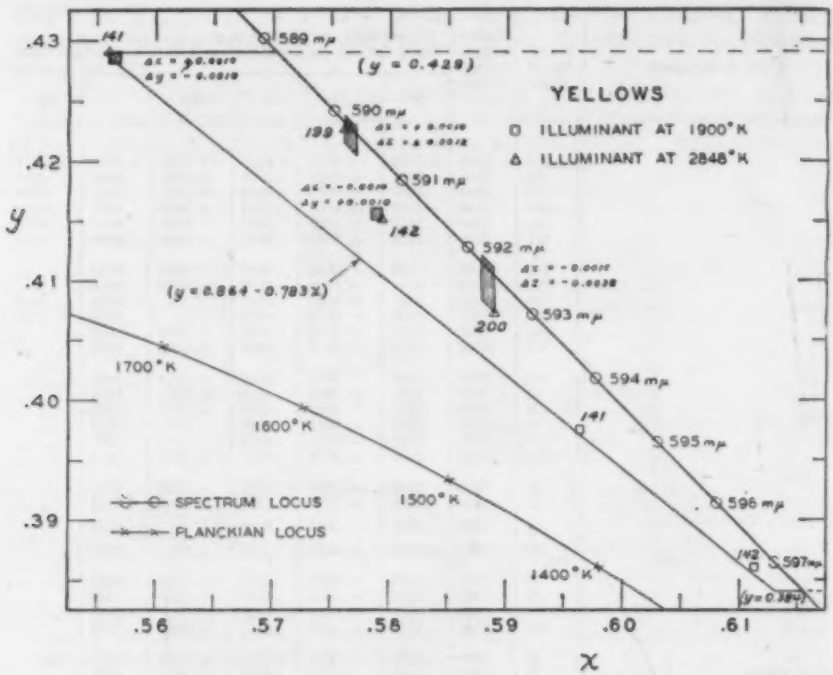

FIGURE 11.—*Large-scale section of figure 8 showing (dark areas) the tolerances in x and y, or x and z, permitted in glasses certified as duplicates of standard limit glasses designated as yellow, for pressed ware and disks.*

time involved in preparing samples and making measurements was greatly shortened, and the issuance of the specifications expedited, by permitting such deviations from what in many cases might be considered a more ideal set of tolerances.

In addition to restrictions on the chromaticities of the duplicates of the standard limit glasses, as shown in table 5, it was also desirable to set tolerances on the values of T_{AAR} for such glasses, and of T_r/T_v for the blue and purple glasses. Accordingly, values were adopted as shown in table 6. The magnitudes of the tolerances were determined largely by the same considerations as were effective for the chromaticity tolerances. In these cases, however, it is no disadvantage to any manufacturer if the T_{AAR} value of his glass is more or less than that of another manufacturer. This is because the manufacturer is required to have an "approved photometer," by means of which the value of T_{AAR} for any glassware can be actually measured from the

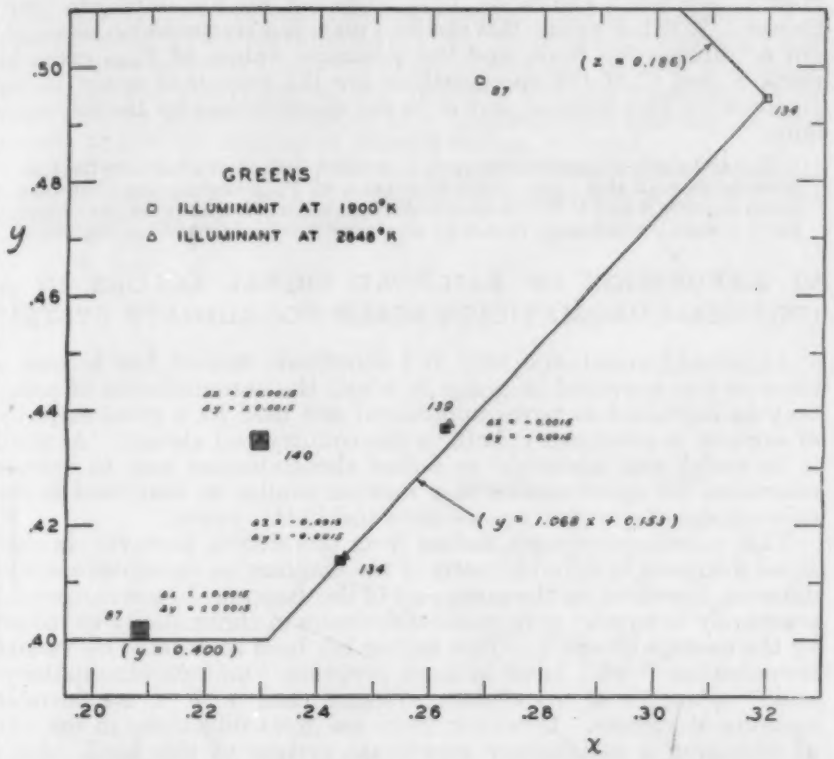

FIGURE 12.—*Large-scale section of figure 8 showing (dark areas) the tolerances in x and y permitted in glasses certified as duplicates of standard limit glasses designated as green, for pressed ware and disks.*

TABLE 6.—*Maximum deviations of luminous transmission on the AAR scale, T_{AAR}, and of red to total luminous transmission, T_r/T_w, both for 2,360° K, permitted for glasses certified as duplicates of standard limit glasses for railroad signaling, AAR Signal Section specifications 69–40 and 59–39*

Color designation	Type	Values of T_{AAR}		Values of T_r/T_w[a]	
		Light limit	Dark limit	Light limit	Dark limit
Red	(69–40, Except highway crossing)	170 ±15	100 ±5		
	Highway crossing	310 ±30	220 ±20		
Yellow	Lantern	250 ±15	145 ±5		
	Non-HR	215 ±10	160 ±5		
	Disk	(b)	(b)		
Green	Lantern	300 ±15	250 ±15		
	Non-HR	205 ±10	150 ±5		
	Disk	190 ±10	138 ±5		
	Lantern	185 ±10	127 ±5		
Blue		130 ±5	75 ±3	0.008 ±0.001	0.000+0.001
	Lantern	125 ±5	56 ±3	.014 ±.002	.008 ±.002
Purple	Kerosine	130 ±5	73 ±3	.120 ±.010	.160 ±.010
	Electric	40 ±3	30 ±2	.190 ±.020	.220 ±.020
Lunar white	Kerosine	122 ±5	80 ±4		
	Electric	200 ±10	147 ±5		

[a] For blue and purple glasses only.
[b] No values specified.

known (certified) values of T_{AAR} engraved on his duplicate limit glasses. In other words, this certified glass is a transmission *standard*, not a transmission *limit*, and the minimum values of T_{AAR} given in parts A and C of the specifications are the ones that apply to his glassware. This is taken care of in the specifications by the following note:

> It may be noted that in some cases a certified dark-limit glass may have, in accordance with this table (table 6) a value of T_{AAR} slightly less than that given in parts A and C of this specification; this does not, however, invalidate parts A and C, which must be met by all glasses to be used in railroad signaling.

VI. EXPRESSION OF RAILROAD SIGNAL COLORS IN A UNIFORM-CHROMATICITY-SCALE COORDINATE SYSTEM

As already noted, the 1931 ICI coordinate system has become a more or less universal language in which the chromaticities of colors may be expressed in terms understood and used by a great majority of workers in colorimetry, both in this country and abroad. As such, it is useful and adequate to define chromaticities and to express tolerances for specifications in a manner similar to that used in the railroad signal specifications as described in this paper.

This coordinate system suffers from one defect, however, in that equal distances in different parts of the diagram, or equal distances in different directions on the same part of the diagram, do not correspond accurately to equally perceptible differences in chromaticity as judged by the average observer. This matter has been considered by various investigators,[21] who have in turn proposed "uniform-chromaticity-scale" triangles or coordinate systems, and with a considerable measure of success. However, there are great difficulties in the way of obtaining a satisfactory coordinate system of this kind. Aside from the question whether any plane surface will give such uniform chromaticity scales, it is known that different systems would be necessitated for differing observing conditions. For example, the same coordinate system will not give equal chromaticity scales for both (1) extremely small sources such as are used in most signal installations and (2) large fields, such as are commonly used in color matching of textiles or in comparing samples with Munsell standards.

Although such investigations are of great interest and may eventually lead to revision of the ICI coordinate system, there is no prospect that such revision will be seriously attempted for a long time. In the meantime, however, it is often instructive to express results in one of these systems to obtain a better idea as to the relative perceptibility of the various colors involved.

The first attempt at transformation of the ICI coordinate system to a uniform-chromaticity-scale coordinate system was made by Judd.[22] As the data on which this transformation was based were obtained with a small (2°) photometric field and with dark surrounds, it is to be expected that this system would be a good approximation to that applicable to signal colors under the usual signaling conditions. In fact, no certain improvement in Judd's system for such a purpose has been made.

[21] See references 721–31 of chapter VII, Quantitative data and methods for colorimetry, of the forthcoming report of the OSA Committee on Colorimetry, J. Opt. Soc. Am. **34**, 633 (1944).

[22] Deane B. Judd, A Maxwell triangle yielding uniform chromaticity scales, J. Research NBS **14**, 41 (1935) RP756; J. Opt. Soc. Am. **25**, 24 (1935).

In this uniform-chromaticity-scale system, the coordinates x, y, z are replaced by new coordinates r, g, b. As in the ICI system, these coordinates represent fractional parts of reddish, greenish, and bluish primaries, but the primaries are different. Judd's paper should be consulted by those interested in a further understanding of this system and of the method of transformation involved.

In figure 13 are shown, on the Judd uniform-chromaticity-scale triangle, essentially the same data as are shown in figure 8. The following points may be noted:

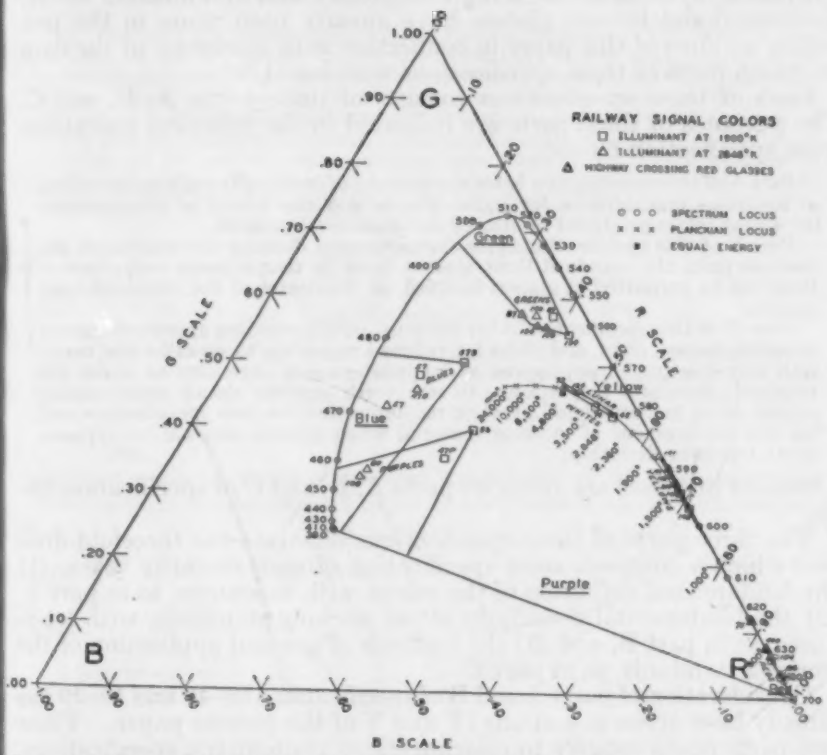

FIGURE 13.—*Transformation of the data of figure 8 to the mixture diagram according to the 1931 ICI standard observer and the Judd uniform-chromaticity-scale triangle.*

Equal distances in this coordinate system are more nearly representative of equally perceptible differences in chromaticity than in the ICI coordinate system.

1. The distance from the red to the yellow signal colors is the same as that from the yellow to the green signal colors.
2. The separation of the lunar whites from the yellows and greens is approximately equal.
3. There is considerable diminution of the area representing permissible green signal colors from the corresponding areas for the other colors.

All these effects are, of course, consistent with the changes from circles of uniform radius on Judd's triangle to ellipses of varying size, eccentricity, and orientation on the ICI diagram, which have been

illustrated elsewhere.[23] They show, furthermore, the excellence of the signal colors selected by the engineers, particularly the choice of the red, yellow, and green signals used for long-range signaling on the main lines, where the trains move at high speed.

VII. AAR SIGNAL SECTION SPECIFICATIONS FOR SIGNAL GLASSES AND HAND LANTERN GLOBES

References to AAR Signal Section specification 69–40, Signal glasses (exclusive of kerosene hand lantern globes), and specification 59–39, Kerosene hand lantern globes, have already been made in the preceding sections of this paper in connection with discussion of the data on which parts of these specifications were based.

Each of these specifications consists of three parts, A, B, and C. The purposes of these parts are indicated in the following quotations from specification 69–40:

> Part A of this specification is for the purpose of defining the minimum values of luminous transmission for signal glasses and the limits of chromaticity for signal colors produced by illuminant-glass combinations.
>
> Part B of this specification is for the purpose of defining the maximum deviations from the standard limit glasses, both in transmission and chromaticity, to be permitted in glasses certified as duplicates of the standard limit glasses.
>
> Part C of this specification is for the purpose of providing approved colored roundels, lenses, discs, and slides for railroad signaling, to describe the materials and specify the appliances and appurtenances necessary to make the required tests and inspection. It sets forth specific detail requirements representing modern signal practice recommended for new installations and for the replacement of existing material when general renewal or replacement becomes desirable.

Similar purposes are given for parts A, B, and C of specification 59–39.

The three parts of these specifications illustrate the threefold division which a complete color specification often necessarily takes: (1) the fundamental definition of the colors, with tolerances, as in part A, (2) the fundamental definitions of the working standards, with tolerances, as in part B, and (3) the methods of use and application of the working standards, as in part C.

Consideration of parts A and B of specifications 69–40 and 59–39 has already been given in sections IV and V of the present paper. These two parts relate entirely to colorimetric or photometric specifications. Part C gives various information pertinent to a purchase specification, as quoted above, and in addition, specifies the transmission tests and the chromaticity tests that are made possible by the certified duplicate limit glasses.

The following excerpts from part C of specification 69–40 describe these tests, and indicate the part that the National Bureau of Standards takes in the certification of duplicate limit glasses.

> **3. Apparatus and appurtenances for testing**
>
> *(a) Certified limit glasses*
>
> 1. Certified light and dark limit glasses, calibrated by the National Bureau of Standards, Washington, D. C., shall be made available by the Seller for use of the Purchaser while conducting tests. These certified glasses

[23] Deane B. Judd, Estimation of chromaticity differences and nearest color temperature on the standard 31 ICI colorimetric coordinate system, J. Research NBS 17, 771 (1936) RP 944; J. Opt. Soc. Am. 26, 421 6).

shall serve to define both the proper luminous transmissions of the glasses to be tested and the proper chromaticities of the resulting signal colors as hereinafter provided.

(b) Photometer

1. An approved photometer shall be made available by the Seller for use of the Purchaser while conducting tests. The illuminant used for measurements shall have a color temperature between 2360°K and 3000°K, and with no samples in the beams the two halves of the photometric field shall have the same chromaticity.

Note.—1. Vacuum tungsten lamps or gas-filled tungsten lamps with white [24] bulbs should give the specified color temperature, if operated at normal voltage.

2. The 1908 specification established spectrophotometric values for a glass in each of the six colors, having a chromaticity and a transmission value approximately midway between the respective values for the light and dark limits. Each of these glasses was given an arbitrary value of 100 percent for use as a standard in laboratory and routine photometry. By means of these standard glasses, the present photometric scale for measuring the transmission of all colored signal glasses was established. This practice is continued, except that the 100 percent pressed standards have been superseded by the standard limit glasses in the form of 2-in. polished squares.

4. Tests and inspection

* * * *

(e) Transmission test

1. The Purchaser shall measure the transmission T_{AAR} of each glass, using the above specified photometer and illuminant and respective certified limit glasses whose values of T_{AAR} are engraved thereupon. A glass shall not be acceptable whose value of T_{AAR} is less than the respective minimum value given in the following table:

Table of minimum values of luminous transmission on the AAR scale, T_{AAR}

Color designation	Pressed lenses and roundels, and cut or pressed slides	Polished flat discs
Red	85	115.
Red (highway crossing)	220	
Yellow	130	(Depolished on one side)
Green	150	135.
Blue	75	
Purple (kerosene)	73	
Purple (electric)	30	30.
Lunar white (kerosene)	80	
Lunar white (electric)	147	

Note.—Either of the following additional tests shall be applied to the blue and purple glasses: (1) a red glass (approximately equivalent to the dark limit red glass) shall be placed over the eye-piece of the photometer. The transmission of blue glasses for this red light shall be not greater than that of the light limit blue glass, and similarly the transmission of purple glasses for this red light shall be not less than that of the dark limit purple glass; or (2) an incandescent lamp shall be viewed through a red glass (approximately equivalent to the dark limit red glass). The test glass and the limit glass, placed edge to edge, shall be rapidly alternated in position in the beam between the lamp and the eye. The transmission of the blue glasses so examined (for red light) shall appear not greater than that of the light limit blue glass, and similarly the transmission of purple glasses so examined (for red light) shall appear not less than that of the dark limit purple glass.

[24] That is, inside-frosted incandescent lamps.

(f) Chromaticity test

1. The Purchaser shall compare the chromaticity of each glass with that of the respective certified limit glasses, using for this purpose the above specified photometer and illuminant. The comparisons shall be made with brightnesses matched. A glass shall not be acceptable if its chromaticity fails to meet either of the following requirements:

(a) The hue shall be not outside the hue limits given by the respective certified limit glasses; except that (1) for red glasses, only the yellow limit need be tested, and (2) for disc green glasses, the blue limit shall be given by the dark limit pressware (non heat-resisting) green glass.

(b) The saturation shall be not less than that given by the respective certified light limit glasses; except that, for lunar white glasses, the saturation shall be not outside the saturation limits given by the respective certified limit glasses.

* * * *

5. Marking

(a) Certified limit glass marking

1. Each certified limit glass (2 in. square or 1 in. diameter disc) shall be permanently engraved with the serial number by the maker and further permanently engraved by the National Bureau of Standards with the serial number, the designation, the value of T_{AAR}, the N. B. S. test number, and the date.

Note.—In all cases, the engravings may be verified, and additional information regarding the certified limit glasses obtained, from the N. B. S. Certificates for the glasses which shall be made available to the Purchaser by the Seller.

Since the formulation of these specifications, over 200 duplicate limit glasses, with certificates, have been issued by the National Bureau of Standards to various applicants, some in foreign countries.

Success in carrying through the program of railroad signal glass standardization described in the previous and present papers has resulted in large measure from the generous cooperation of Corning Glass Works. All the field tests conducted by the signal engineers in their selection of colors and glasses have been held at Corning. Special acknowledgment is due in this connection to H. P. Gage, under whose supervision these tests were conducted and who has had charge of the preparation of the hundreds of glasses prepared during this work, either for study or for issuance as certified duplicate glasses.[25] The authors have also had the valuable technical advice of Dr. Gage throughout the work.

In conclusion, reference should again be made to the progressive spirit of the railroad signal engineers, which has kept them among the leaders in the use of the best technics in the selection of signal colors and in the formulation of purchase specifications based on colorimetric data. Credit for the present satisfactory status of the railroad signal glass specifications is largely due to (1) the chairman of AAR Signal Section Committee VI, J. C. Mock, under whose supervision the initial program was started, and A. S. Haigh, who carried on after the retirement of Mr. Mock and brought the specifications to their present status, and (2) the secretaries of the Signal Section, H. S. Balliet at the start of the work and his son, R. H. C. Balliet, in whose office the preparation and revision of the specifications have been handled.

WASHINGTON, August 31, 1945.

[25] Many of the glasses certified by the National Bureau of Standards have been prepared by Corning Glass Works without charge. Under present arrangements such glasses may be purchased from Corning Glass Works for a nominal amount and certified by the National Bureau of Standards at regular test-fee schedules. The Bureau will also accept suitable glasses from other companies for test, with the regular charge for certification or rejection.

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ATTACK ON REFRACTORY CLAY POTS BY OPTICAL GLASSES

By Willard H. Parsons and Herbert Insley

ABSTRACT

Examinations were made of the walls and bottoms of approximately 200 refractory clay pots of lined and unlined types to determine the extent of penetration of optical glasses into refractory material. Examinations made with a petrographic microscope of samples of unused pot bottom indicated the structure of the heat-treated refractory. Similar examinations of selected samples from the bottoms of 62 used pots revealed the manner of attack by corrosive glasses and identified the crystalline and glassy reaction products formed. These reaction products were found at the interface between refractory and glass and within pot bottoms penetrated by glass. The pots were used in the manufacture of barium crown, barium flint, light crown, borosilicate crown, and several different flint optical glasses.

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I. INTRODUCTION

In the manufacture of optical glasses in refractory clay pots, reactions occur along the pot-glass interface at high temperatures. When such reactions attain considerable magnitude, not only the quality of the glass may be affected in regard to its optical properties,

striae, or seed content, but also the pot is damaged. In some instances, failure of the pot to hold the melt may result.

The purpose of the present investigation was to determine the manner and extent of attack on the refractory by optical glasses of different compositions and to identify the accompanying reaction products.

Examinations were made visually of the walls and bottoms of pots after the production of glass to reveal the extent of penetration of glass into the refractory. Samples for detailed microscopic study were collected showing both corroded and noncorroded regions of the pot bottom. The pots were used in the manufacture of barium crown, barium flint, light crown, borosilicate crown, and several different flint optical glasses.

II. REFRACTORY CLAY POTS

The clay pots investigated were made, cured, and used in the production of optical glass at this Bureau. Details on the manufacture and the physical properties of the pots are given by Heindl, Massengael, and Cossette [1].[1] The batch composition and the chemical analysis of most of the pots are given in table 1. Four semisiliceous pots contained powdered flint, in addition to the batch materials listed in table 1, in quantity sufficient to bring the SiO_2 content of the heat-treated pots to approximately 68 percent [1]. One semisiliceous pot contained quartz sand in place of powdered flint.

Examinations were made of two types of pots, lined and unlined. The two were alike, except that the walls and bottoms of the lined pots had a coating, about ⅛ in. thick, of relatively fine-grained material with a composition similar to that given in table 1. Two pots contained alumina-rich linings whose raw batch materials included alumina, prepared mullite, ball clay, and kaolin [1].

TABLE 1.—*Composition of refractory clay pots used in the production of optical glass*

Raw batch composition [a]		Chemical analysis of heated refractory [b]	
Material	Amount	Oxide	Amount
	Percent		*Percent*
Maine feldspar	6.0	SiO_2	59.5
Tennessee ball clay	10.0	Al_2O_3 [c]	35.6
Kentucky ball clay	10.0	Fe_2O_3	0.78
North Carolina kaolin	12.5	TiO_2, ZrO_2, etc.	.8
Delaware kaolin	4.5	CaO	(d)
Georgia kaolin	4.5	MgO	.1
Pot shell grog	52.5	Na_2O	.66
		K_2O	2.7
	100.0	Ignition loss	0.15
			100.09

[a] From Heindl, Massengale, and Cossette [1].
[b] Analyst: I. Mockrin, National Bureau of Standards.
[c] Determined as R_2O_3 minus Fe_2O_3 and TiO_2, ZrO_2, etc.
[d] Less than 0.1 percent.

The pots were preheated in furnaces for about 60 hours, during which time the temperature was raised gradually from near 100° to 1,350° or 1,400° C. The pots were then transferred to glass-melting

[1] Figures in brackets indicate literature references at the end of this paper.

furnaces where they remained for 19 to 26 hours during the melting and fining of the different optical glasses. The temperatures within the furnaces ranged from 1,350° to 1,450° C,[1] depending on the schedule for the type of glass being produced. These temperatures were maintained for 8 to 20 hours, after which they were lowered gradually to pot-exit temperatures between 950° and 1,100° C.

III. PROCEDURE

The walls and especially the bottoms of about 200 pots were inspected when the pot body was separated from the glass. For the present investigation, a selection was made of pots that in most instances had leaked in the furnaces or were cracked and penetrated by glass. Such pots probably best showed the effects of glass attack on the refractory. Samples, for detailed microscopic examinations, were collected from the bottoms of 62 pots. These samples included the pot-glass interface as well as refractory penetrated by the melt. Additional samples were obtained from a few pot bottoms not penetrated by glass. Unless otherwise stated, all references to the refractory apply to samples from the bottoms of pots. All samples were examined in thin section and some also in powdered form with a petrographic microscope. Preston [2] has suggested a similar microscopic procedure for the examination of pots.

IV. VISUAL EXAMINATIONS OF USED POTS

Visual examinations revealed that the more porous refractory of unlined pots was deeply penetrated by barium crown and barium flint glasses (fig. 1). Glass not only filled and enlarged existing pores, but also formed continuous channels, with a maximum diameter of ½ in., which sometimes continued entirely through the bottom. The glass that penetrated into the pores and small channels was colored a pale yellow, but the glass filling the larger channels was essentially colorless. The walls were not penetrated except within 4 to 5 in. of the bottom.

The extremely reactive or corrosive nature of the ingredients of barium glasses under certain conditions was illustrated during the manufacture of a barium crown glass in which the batch materials were added in two lots: first, the least corrosive and later, the more corrosive (boron, zinc, lead, arsenic, antimony, and that part of the barium added as nitrate). Just after the second lot of batch material was added, the melt bubbled up and spilled over. The molten material that ran down the outside of the pot corroded channels, or grooves, ¼ to ⅜ in. deep in the walls.

Borosilicate crown and most of the flint glasses usually did not penetrate the unlined pots. Sometimes pores just below the pot-glass interface were filled or partly filled with glass, but penetration rarely occurred to a depth of more than ½ in. An exception was a flint glass with 62 percent of PbO, which sometimes penetrated as much as 2 in. Any flint glass that did penetrate into the pores and small channels was colored a deep yellow, although the glass in large channels or cracks was essentially colorless.

The lined pots revealed no evidence of attack by any type of glass

[1] The maximum temperature for one special melt of barium crown was only 1,200° C.

on the typical [3] lining. Despite this resistance to glass attack, the lining did not always protect the main part of the pot bottom. Cracks and voids in the lining permitted glass to make contact with the underlying more porous refractory (fig. 2). When such flaws occurred, barium glasses spread laterally beneath the lining as much as 6 in. Borosilicate crown and flint glasses filled cracks in the lining, but did not penetrate or spread over ½ in. into the main refractory material with the occasional exception of the flint glass containing 62 percent of PbO. Cracks in the walls, except in the lower 3 or 4 in., did not result in glass penetration. Two alumina-rich linings, however, showed visual evidence of moderate reactivity with molten glass by a change in color and luster of the lining material.

Many seeds of various sizes were observed in glass-filled pores, channels, and cracks in both lined and unlined pots. Examinations were made visually and with the aid of a binocular microscope (magnification about 12 times) of samples from 25 pots in an effort to determine the origin of these seeds. In areas penetrated by glass, all pores in the refractory were not completely filled. Some pores were coated by a thin layer of glass (fig. 3, A). Others were considerably enlarged and contained numerous small seeds (fig. 3, B).

The seed rating of the glass was compared with the extent of cracking of the pot bottom for 137 barium melts. Some 111 of the melts were produced in uncracked or only slightly to moderately cracked pots. Of these melts, 35 percent were very seedy. The remaining 26 melts were produced in pots with badly cracked bottoms, and 61 percent were very seedy.

V. MICROSCOPIC EXAMINATIONS OF SPECIMENS FROM POT BOTTOMS

1. STRUCTURE OF UNUSED POTS

Heat-treated unlined pots in which no glass was melted contained a relatively large number of pores, as illustrated by figure 4. The pores were of two kinds: large (1 to 3 mm in average diameter), spherical pores (fig. 1) and numerous, narrow, channel-shaped openings (figs. 2 and 4). A majority of the larger of these channels were oriented with their long dimensions essentially vertical. The linings were only about one-sixth as porous as the main refractory materials [1]. The pores in the lining were small (0.1 mm in maximum diameter) and more or less spherical in shape (fig. 5).

The pot bodies were composed largely of a glassy bond containing numerous needlelike crystals of mullite. The mullite needles in the more porous refractory were relatively long (maximum 30 microns) and narrow (1 to 2 microns). They were often spaced irregularly, but were arranged sometimes in 60° networks. In the lining the mullite needles were similar but smaller. Grog grains contained a higher proportion of mullite and were often darker in color than the surrounding material (fig. 5). Infrequent, small, irregular, isotropic grains (5 to 10 microns in diameter) of glassy or amorphous material showed no evidence of mullite growth. Occasional small quartz grains with visible solution rims were also present.

[3] Where necessary for clarity, linings or pots of the composition given in table 1 are referred to as typical linings or pots.

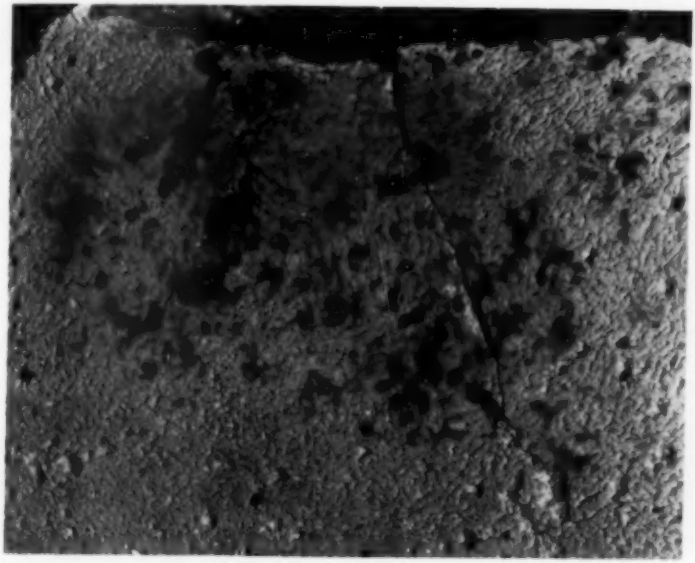

FIGURE 1.—*Bottom of unlined pot penetrated by glass.*

Refractory-glass interface at top. Dark areas are glass. Glass-filled pores are greatly enlarged and connected as compared with unpenetrated pores in lower part of photograph. (Crack formed during cutting of specimen.) Magnification, × 1⅓.

FIGURE 2.—*Bottom of lined pot penetrated by glass through cracks in lining.*

Lining-glass interface at top. Gray areas are glass; black areas, open spaces. The glass has spread in the more porous refractory after passing through the lining along two small cracks. Observe elongated shape and vertical orientation of pores. Magnification, × 2½.

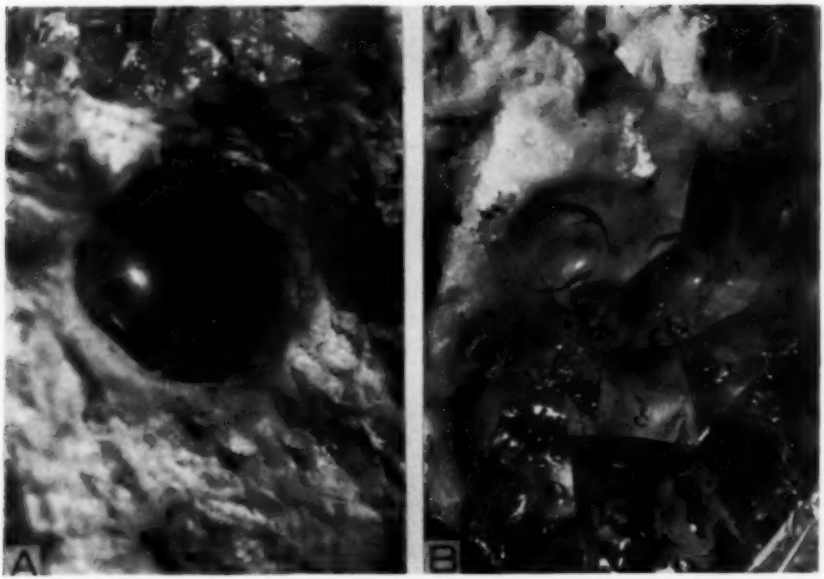

FIGURE 3.—*Seeds in pot bottom penetrated by glass.*

A, Gas bubble in refractory coated on inside with glass forming a large stationary seed. Magnification, × 7. B, Several small seeds in a glass-filled channel in the refractory. Magnification, × 12.

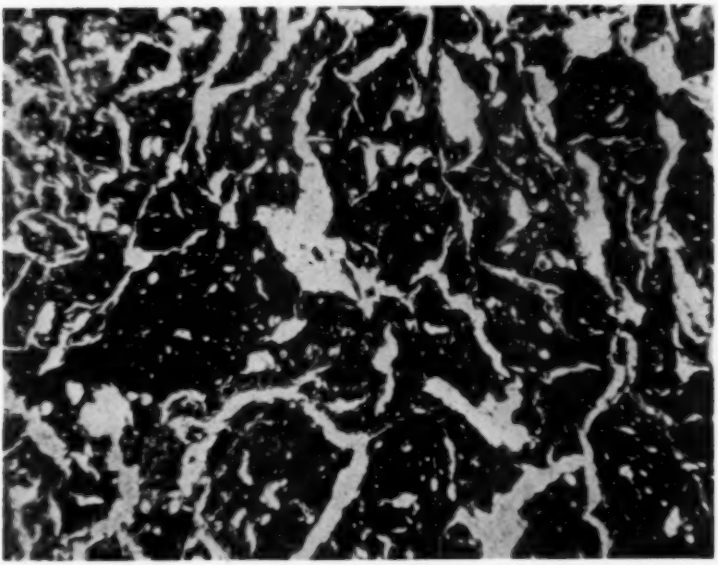

FIGURE 4.—*Bottom of heat-treated unlined pot before production of glass.*

Note channel-like character and essentially vertical orientation of pores (white). Ordinary light. Magnification, × 24.

FIGURE 5.—*Glass-filled crack in bottom of lined pot.*

Observe structure of lining and contact (arrows) of lining (above) with the more porous refractory (below). Opposite walls of the crack match each other. Black areas are grog grains; white area of the crack and of pores connected to it (lower left) is glass; white of the other pores is open space. Ordinary light. Magnification, × 18.

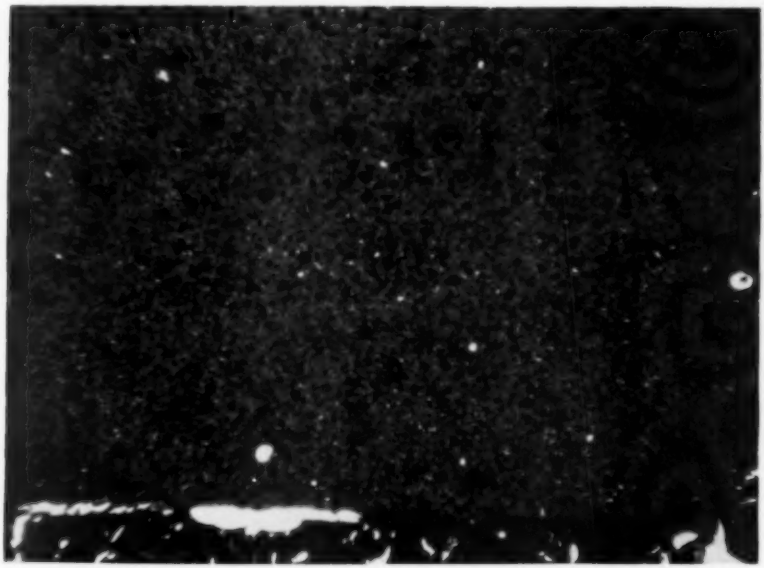

FIGURE 6.—*Heat-treated alumina-rich lining before production of glass.*

More porous refractory at bottom. Dark spots are aggregates of corundum crystals; gray areas are a mixture of mullite and glassy bond; white specks and areas are pores. Ordinary light. Magnification, × 24.

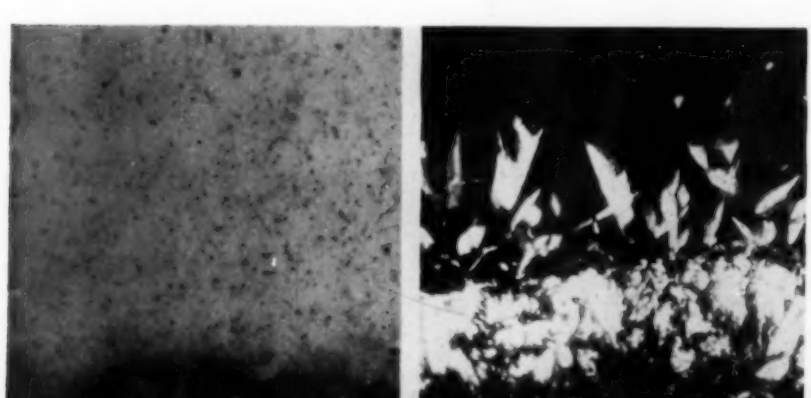

FIGURE 7.—*Lining-glass interface of a BaC 6109 melt.*

A, Glass above, lining below. Reaction crystals are invisible because they have a refractive index near that of the glass. Ordinary light. B, Same field as A but with crossed nicols. Double layer of barium-feldspar crystals visible (white). White grains in the lining are mullite crystals. Magnification, × 210.

The semisiliceous pots were similar to the typical pots in appearance and mineral composition with the addition of numerous well dispersed, sharply angular quartz grains. The quartz grains averaged from 10 to 40 microns in diameter, with a few up to 70 microns, in the pots made with powdered flint and about 200 to 300 microns (0.2 to 0.3 mm) in the pot made with quartz sand. Many grains had a narrow reaction rim (1 to 2 microns wide) of a dense isotropic material, possibly cristobalite.

The alumina-rich linings, which had a tendency to crumble when examined, consisted of many minute aggregates (30 to 80 microns in diameter) of fine-grained corundum crystals surrounded by mullite and a glassy bond (fig. 6). The mullite occurred in two different textures: prismatic crystals (5 by 15 microns in average dimensions), which corresponded in grain size and appearance to the prepared mullite in the batch, and needles (about 10 microns long by 1 micron or less in thickness) in glass.

2. STRUCTURE AND REACTION PRODUCTS OF USED POTS

The results of the microscopic examinations of pots attacked by 16 different optical glasses are summarized in table 2. The observations are described in further detail in this order: first, the reaction rim at the pot-glass interface and, second, refractory penetrated by glass. The individual optical glasses are designated by numbers which correspond to that portion of the value for the index of refraction which lies to the right of the decimal point plus these abbreviations: BaC=barium crown, BF=barium flint, LC=light crown, BSC=borosilicate crown, and F=flint.

(a) BARIUM GLASSES

(1) *BaC 6109 and BaC 617.*—A reaction rim 0.15 to 0.2 mm in thickness at the interface on both lined and unlined pots consisted of closely spaced barium feldspar (celsian, $BaAl_2Si_2O_8$) crystals without good external form. An upper layer was observed in two pots, which consist of well-developed, bladed crystals extending into the glass (fig. 7).

Below the pot-glass interface, many of the very small channels contained numerous long mullite ($Al_6Si_2O_{13}$) needles. Barium feldspar and barium disilicate (sanbornite, $BaSi_2O_5$) in prismatic crystals and zinc spinel [4] (gahnite, $ZnAl_2O_4$) in well-formed, colorless, octahedral crystals occurred along the walls of other channels (figs. 8 and 9). Zinc spinel was not observed when the melts contained less than 2.5 percent of ZnO (table 2). The crystals were in a glass with a variable index of refraction as low as 1.54 but averaging 1.57. Glass in very large channels or cracks contained no crystals and had an index of refraction about 1.61, approximately that of the original glass.

The indices of refraction of both the barium feldspar and the barium disilicate were slightly lower than those of the pure com-

[4] The optical identification was checked experimentally as follows: 4-g samples of four individual glasses (BF 584, BaC 5725 without ZnO, a glass with 20 percent of BaO and no ZnO, and a glass with 20 percent of ZnO and no BaO) were powdered and mixed thoroughly with equal weights of powdered pot shell. Each mixture was heat-treated separately to approximately 1,400° C for 2 hours and then cooled slowly. Octahedral crystals were found in the two preparations containing ZnO and not in the other two. An X-ray diffraction pattern of these crystals showed them to be zinc spinel.

TABLE 2.—*Reaction products between refractory clay pots and optical glasses of various compositions*

Number of pots examined	Type of glass [a]	Approximate partial glass composition [b]						Maximum melting temperature	Reaction products at the pot-glass interface (in approximate order of abundance)	Reaction products within glass-penetrated pot bottom (in approximate order of abundance)	Approximate lowest index of refraction of glass which has penetrated the pot bottom [a]
		BaO	ZnO	PbO	SiO_2	K_2O	Na_2O				
BARIUM GLASSES											
2	BF 564	% 13	% 8	% 19	% 50	% 8	% 2	°C 1,400	Traces of nephelite-kaliophilite S. S.[i] and cristobalite.	Barium feldspar, zinc spinel, cristobalite, mullite, trace of corundum.	1.51
4	BF 604	14	8	23	46	8	0	1,410 to 1,425	Cristobalite, trace of kaliophilite	Mullite, barium feldspar, barium disilicate, cristobalite, zinc spinel, trace of corundum.	1.52
3	BaC 5725 [d]	17	0	4	52	0	8	1,350 to 1,390	Barium feldspar	Barium feldspar, mullite, barium disilicate.	1.51
1	BaC 541	20	4	0	59	10	3	1,410	Nephelite-kaliophilite S. S., cristobalite.	No penetration of lined pot bottom	
2	BF 568	28	8	6	46	6	2	1,400	Barium feldspar, cristobalite	Mullite, barium feldspar, barium disilicate, zinc spinel, cristobalite, corundum.	1.51
15	BaC 5725	30	7	0	48	7	1	1,400 to 1,445	Cristobalite (two layers), barium feldspar.	Barium feldspar, mullite, barium disilicate, zinc spinel, corundum, trace of cristobalite.	1.51
10	BaC 6109 [e]	43	[h] 4	tr	39	0	0	[i] 1,350 to 1,425	Barium feldspar (two layers in some pots).	Barium feldspar, mullite, barium disilicate, zinc spinel.[k]	1.54
1	BaC 617 [f]	45	6	1	37	0	tr	1,400	Barium feldspar	Barium feldspar, mullite, barium disilicate, trace of zinc spinel.	
CROWN AND FLINT GLASSES											

2	LC 523 [a]	0	0	0	71	2	15	1,450	Trace of corundum	Mullite, corundum	1.50
1	BSC 511	0	0	0	69	15	8	1,400	Nephelite-kaliophilite S. S. (with oriented inclusions), carnegieite S. S.	do	
7	BSC 517	0	tr	0	66	12	8	1,400	Nephelite-kaliophilite S. S. (with oriented inclusions in some pots), carnegieite S. S., trace of corundum.	do	1.495
2	F 5795	1	0	36	53	10	tr	1,400	Trace of cristobalite	No penetration of lined pot bottom	
1	F 605	0	0	41	48	9	2	1,390	do	do	
4	F 617	0	0	43	46	5	6	1,350 to 1,390	Nephelite-kaliophilite S. S. (with oriented inclusions in some pots), carnegieite S. S., cristobalite, trace of corundum.	Mullite, corundum	1.55
2	F 620	0	0	45	46	5	4	1,390	Nephelite-kaliophilite S. S. (with oriented inclusions), carnegieite S. S., cristobalite, trace of corundum.	do	1.60
3	F 649	0	0	51	41	6	1	1,400	$\alpha KAlSiO_4$ S. S. or $KAlSiO_4$ glass, nephelite-kaliophilite S. S. (with inclusions), traces of cristobalite and corundum.	do	1.60
2	F 720	0	0	62	34	4	0	1,400	$KAlSiO_4$ glass and kaliophilite (with various inclusions).	One or more lead aluminum silicates of undetermined composition, mullite, corundum, cristobalite, trace of metallic lead.	1.60

[a] Optical glasses are designated by numbers which correspond to that portion of the value for the index of refraction which lies to the right of the decimal point plus these abbreviations: BF=barium flint, BaC=barium crown, LC=light crown, BSC=borosilicate crown, and F=flint.
[b] Included here are only those oxides which sometimes enter into the crystalline pot-glass reaction products.
[c] Numbers to the right of the decimal are comparable with those given under "type of glass."
[d] An experimental composition. Also contains 8 percent of CaO.
[e] Also contains 4 percent of Al_2O_3.
[f] Also contains 5 percent of Al_2O_3.
[g] Also contains 9 percent of CaO.
[h] ZnO content variable: 4 percent in 6 melts; 0 percent, ½ percent, 2½ percent, and 8 percent, respectively, in the other 4 melts.
[i] Maximum temperature of 1 special melt was 1,200° C.
[j] S. S.=solid solution or mixed crystals.
[k] Present in those melts with 2½ percent or more of ZnO.

pounds, possibly because of a small amount of $KAlSi_3O_8$ and of alkaline disilicate, respectively, in solid solution [3].

(2) *BaC 5725.*—A multiple reaction rim about 0.1 mm in thickness was present in typical lined and unlined and semisiliceous unlined pots. This rim was more uniform in width on the lined pots. An upper layer of "pine-tree," or skeletal, crystals of cristobalite (SiO_2) extended into the glass (fig. 10), next below was a dense, isotropic layer of the same compound, and finally a lower uneven zone of barium feldspar and partially dissolved refractory material. Only one layer, the barium feldspar zone, was found in pots containing an experimental composition BaC 5725 glass (17 percent of BaO, see table 2).

Reaction zones were not formed along the walls of cracks in the typical linings. In alumina-rich linings, however, barium feldspar laths (fig. 11) and small octahedrons of zinc spinel replaced the mullite and glassy bond but not the corundum of the refractory.

The crystalline reaction products in glass-filled channels in the more porous refractory were the same as those formed by BaC 6109 glass plus occasional traces of very thin corundum (Al_2O_3) plates and cristobalite. The same reaction products occurred in about the same quantity in semisiliceous pots. No zinc spinel was formed by BaC 5725 glass of the experimental composition. Two glasses were present in some large channels. Glass next to the channel walls contained reaction crystals and numerous seeds and had a variable index of refraction (minimum about 1.51). Glass in the middle of the channels was free of crystals, contained only a few seeds, and had an index of refraction about 1.57.

(3) *BaC 541.*—A reaction rim about 0.1 mm in thickness consisted of two parts. Cristobalite crystals with typical pine-tree forms extended into the glass. The lower layer, yellowish brown in color, consisted of nephelite-kaliophilite solid solution ($\beta NaAlSiO_4$-$\beta KAlSiO_4$) with a possible trace of carnegieite solid solution ($\alpha NaAlSiO_4$-$\alpha KAlSiO_4$) [4]. No glass penetrated below the lining-glass interface.

(4) *BF 584, BF 604, and BF 588.*—Single reaction rims, which were thin and irregular in width, occurred with BF 584 and BF 604 glasses. These rims were composed of isotropic cristobalite containing partly dissolved refractory constituents and traces of nephelite-kaliophilite solid solution crystals. A double rim, thicker (about 0.1 mm) and more uniform in width, occurred with BF 588 glass. This rim had an upper layer of pine-tree cristobalite crystals and a lower layer of bladed barium feldspar extending into the refractory.

Below the interface, barium feldspar and barium disilicate (figs. 12 and 13), mullite (fig. 14), zinc spinel (fig. 15), and cristobalite (fig. 16) were in abundance and corundum in small amounts. Two glasses were present with a sharp line of demarcation (fig. 15) or a zone of cristobalite crystals (fig. 16) between them. One glass had indices of refraction below 1.53 and contained the reaction crystals and numerous seeds. The other glass resembled the melt in refractive index and was free from crystals.

The following observations apply to all barium glasses that penetrated below the interfaces or through cracks in the linings. The original elongated pores of the refractory were filled by glass, and most of them were considerably enlarged into continuous, winding channels with many branches and interconnections (figs. 8 and 17). The re-

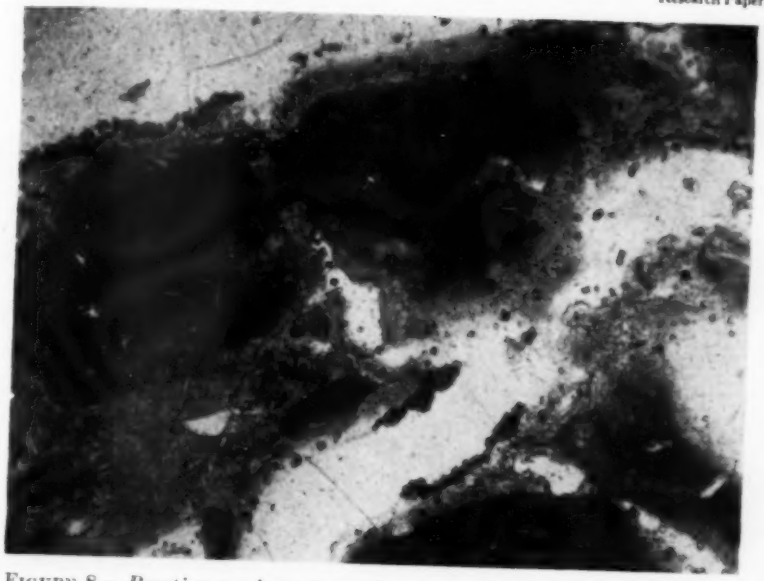

FIGURE 8.—*Reaction products in pot bottom penetrated by BaC 6109 glass.*

Small octahedral crystals of zinc spinel (dark grains with light centers) are within and at borders of glass-filled channels. The grog grains appear less corroded than the rest of the refractory. White areas are glass; black, grog; gray, remainder of refractory and reaction products. Ordinary light. Magnification, × 115.

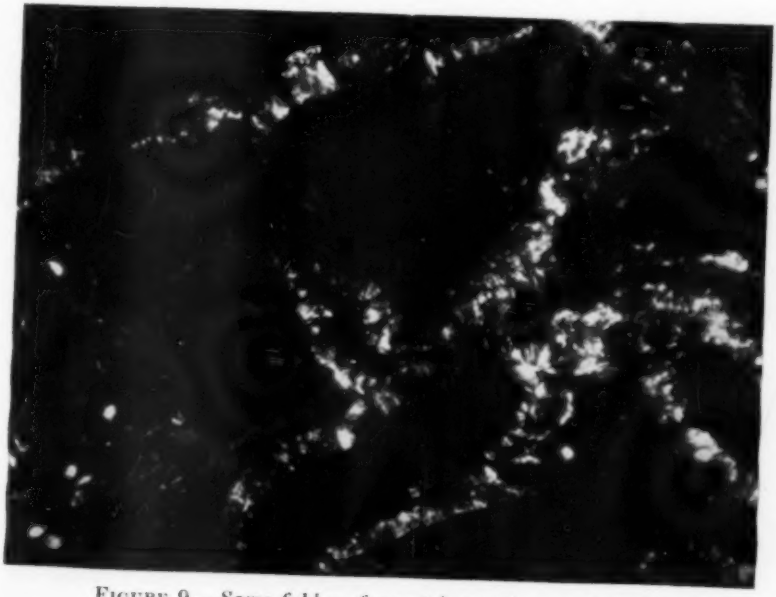

FIGURE 9.—*Same field as figure 8 but with crossed nicols.*

Doubly refracting barium feldspar crystals (white) are at borders of glass-filled channels (black). Cloudy areas are refractory; the cloudiness is due to masses of fine needles of mullite, which are most numerous in the grog grains. Magnification, × 115.

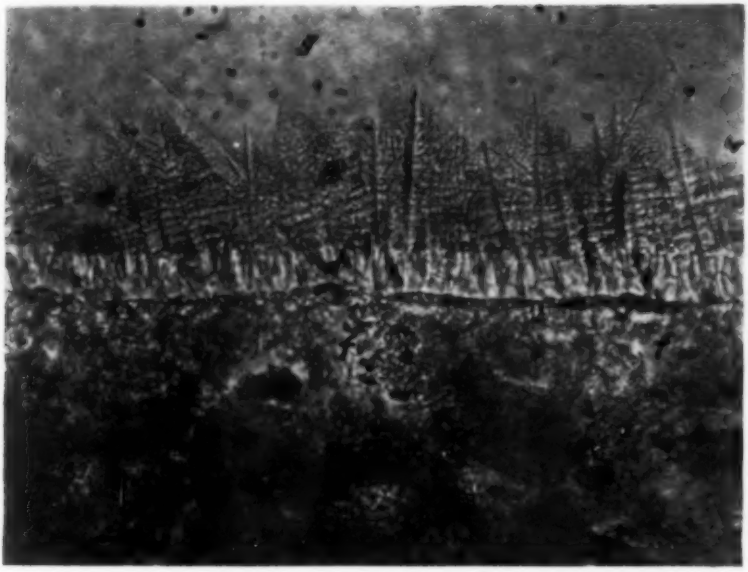

FIGURE 10.—*Lining-glass interface of a BaC 5725 melt.*

g, Glass; p, layer of "pine-tree" cristobalite crystals; d, layer of dense cristobalite; f, masses of barium feldspar filling penetrated regions in the refractory. Ordinary light. Magnification, × 520.

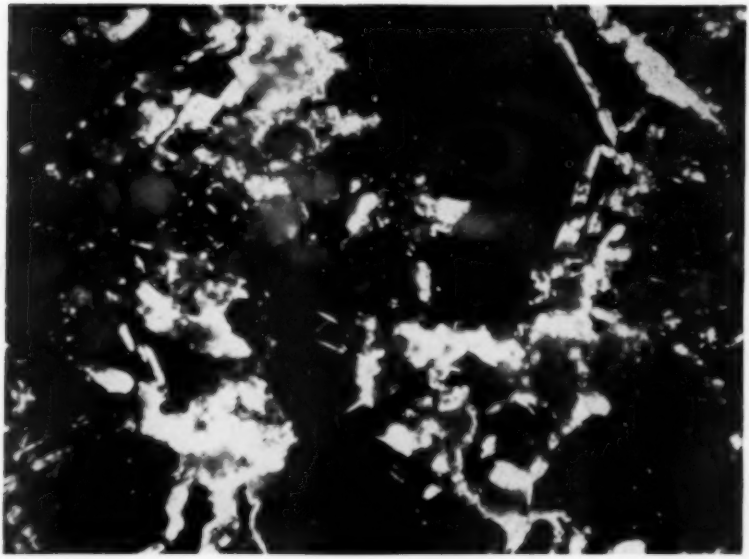

FIGURE 11.—*Alumina-rich lining penetrated by BaC 5725 glass.*

White areas are doubly refracting crystals of barium feldspar; black, glass; gray, aggregates of corundum of the original lining (see fig. 6). Crossed nicols. Magnification, × 100.

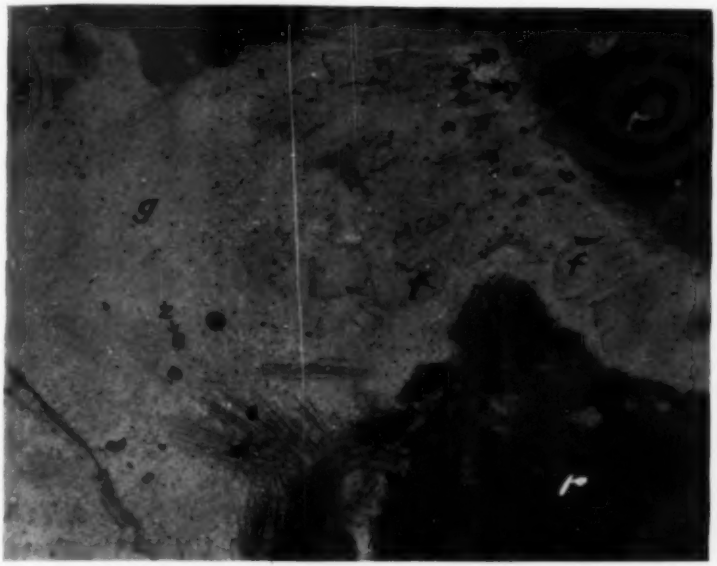

FIGURE 12.—*Reaction products in pot bottom penetrated by BF 604 glass.*

d, Prismatic barium disilicate crystals; f, barium feldspar crystals; z, octahedral zinc spinel crystals; r, refractory material; g, glass; s, seed in glass. Ordinary light. Magnification, × 115.

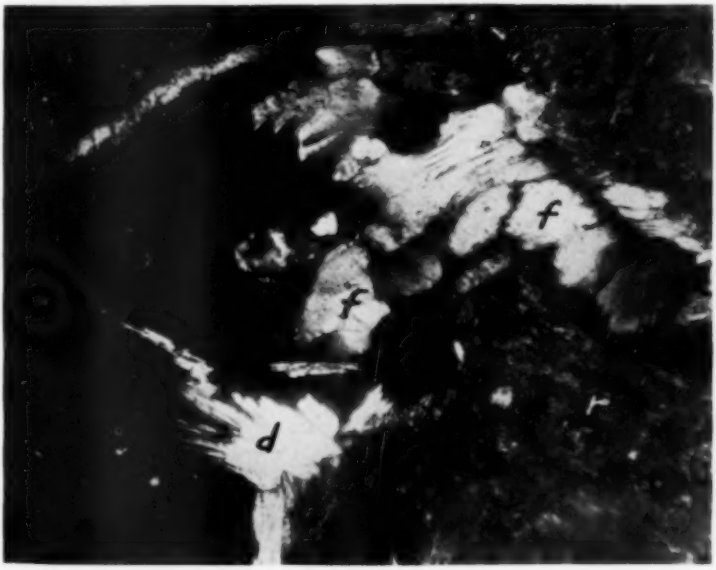

FIGURE 13.—*Same field as figure 12 but with crossed nicols.*

d, Barium disilicate; f, barium feldspar; r, refractory material. Black areas are glass. White specks in the refractory are mullite needles. Magnification, × 115.

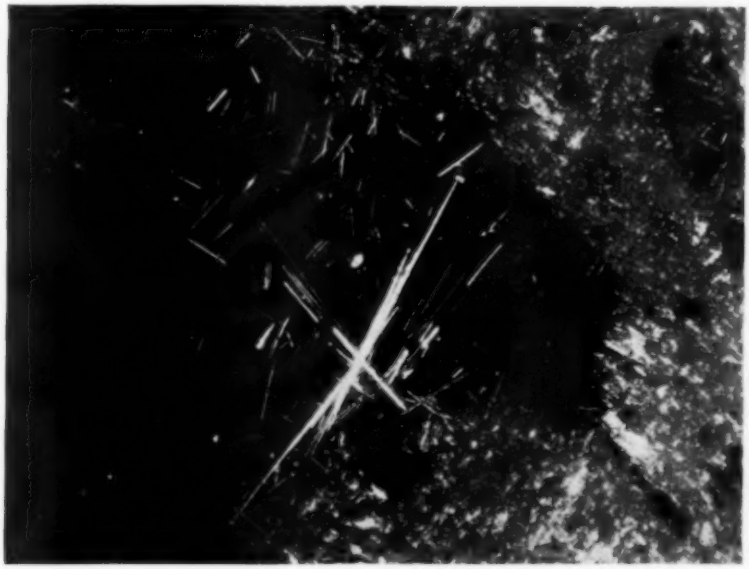

FIGURE 14.—*Mullite needles in pot bottom penetrated by BF 604 glass.*

Dark areas are glass; white lines are mullite needles; light areas are refractory in which the white specks are mullite. Crossed nicols. Magnification, × 115.

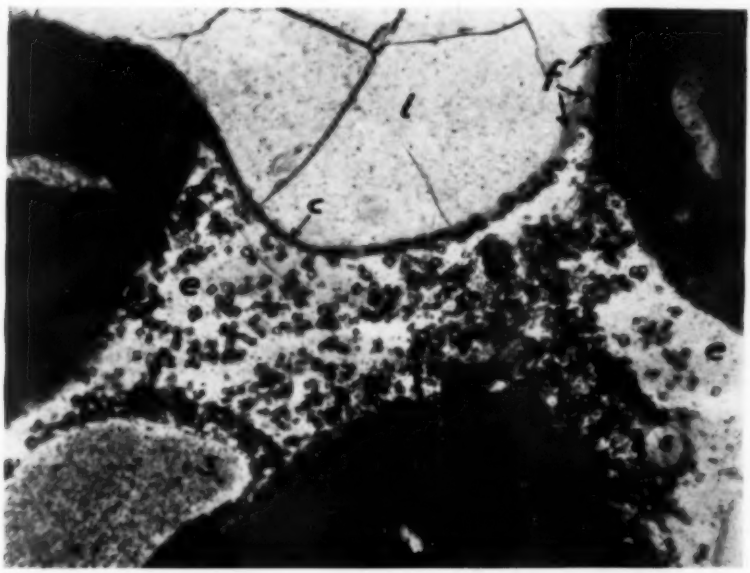

FIGURE 15.—*Contact of two glasses in pot bottom penetrated by BF 604 glass.*

e, Earlier glass containing octahedral crystals of zinc spinel; l, later glass; c, contact of the two glasses; f, film of earlier glass along refactory material (dark areas); s, seeds. Curve of the contact of the two glasses suggests that the later glass pushed against the earlier glass. Ordinary light. Magnification, × 115.

FIGURE 16.—*Cristobalite at two-glass contact along wall of large glass-filled channel in pot bottom penetrated by BF 604 glass.*

r, Refractory; e, earlier glass containing a few zinc spinel crystals; c, coarse-grained cristobalite crystals; f, fine-grained "pine-trees" of cristobalite; l, later glass. Ordinary light. Magnification × 115.

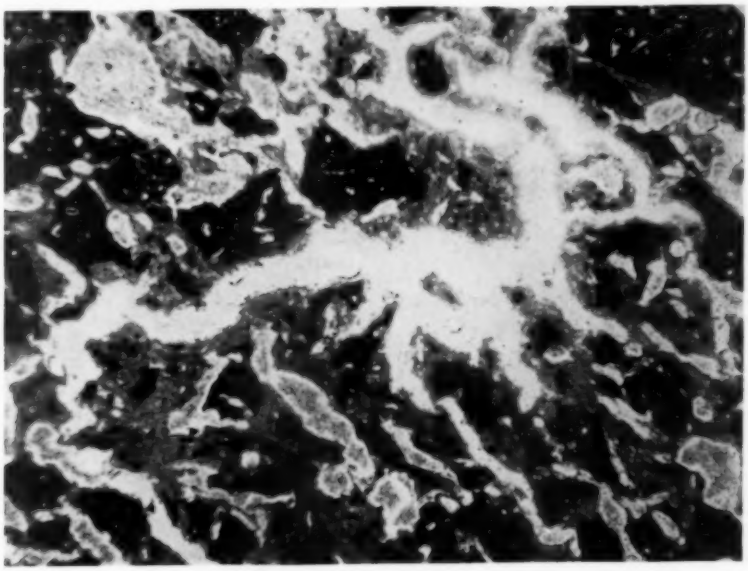

FIGURE 17.—*Pot bottom penetrated by barium glass.*

Branching channels were formed by corrosion of walls of original elongated pore spaces (compare with fig. 4). Grog grains appear less attacked than the rest of the refractory. White areas are glass; black, grog; gray, remainder of refractory. Ordinary light. Magnification × 24.

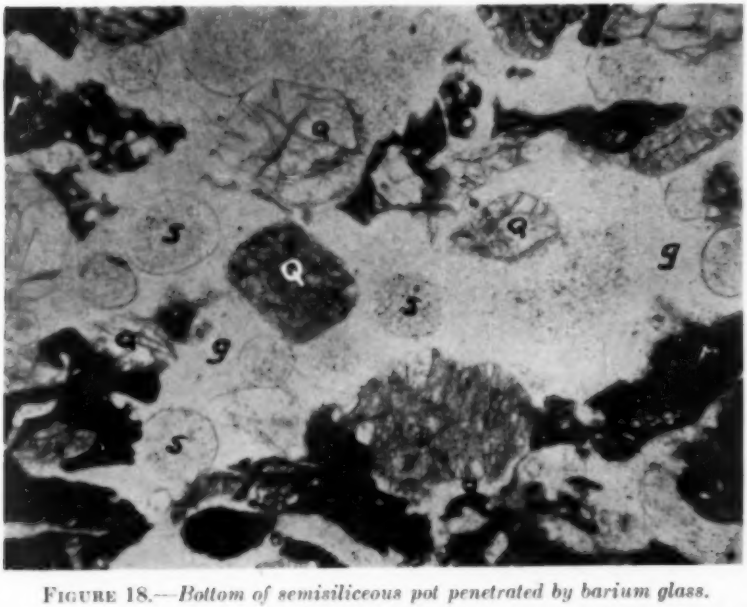

FIGURE 18.—*Bottom of semisiliceous pot penetrated by barium glass.*

The aluminous portion of the refractory has been dissolved by glass leaving quartz grains. Observe numerous seeds in the glass. r, Aluminous part of refractory; q, quartz of refractory; g, glass; s, seeds. Ordinary light. Magnification, × 50.

fractory material along the walls of these channels was partly corroded and filled with reaction crystals, chiefly mullite. The walls between channels were sometimes entirely dissolved to form the large glass-filled spaces seen previously by visual examination (fig. 1).

The grog grains in the refractory were less corroded than the bond and often appeared in thin section as islands in the larger channels (fig. 17). Small channels were observed between grog particles, but not through such particles (fig. 8). The quartz grains of the semisiliceous pots presented a similar appearance (fig. 18).

Cracks through the lining were mechanical in origin, as indicated by complimentary irregularities in the opposite sides (fig. 5).

No apparent relation existed between the maximum melting temperature or its duration and the character of the channels and reaction products. For example, the maximum temperatures of the 10 BaC 6109 melts ranged from 1,200° to 1,425° C. The pot in which glass was melted at 1,200° C contained numerous channels and the same reaction products as the pots heated at higher temperatures.

(b) CROWN GLASSES

(1) *LC 523.*—No well-defined reaction rim occurred. A few small corundum plates were scattered along the interface.

Pores in the refractory which were filled with glass were neither noticeably enlarged nor connected into continuous channels. A few reaction crystals of mullite and corundum gave the only evidence of pot attack. The maximum scheduled melting temperature, 1,450° C, was the highest of that for any glass.

(2) *BSC 511 and BSC 517.*—A double reaction rim was about 0.1 mm in maximum thickness (fig. 19). An upper layer consisted of intricately twinned crystals of carnegieite $\alpha KAlSiO_4$ solid solution, and a lower layer contained nephelite-kaliophilite solid solution. Some of the nephelite solid solution contained fine, oriented inclusions (fig. 20) which might be TiO_2, Fe_2O_3, or both. These inclusions were derived probably from the constituents of the refractory and imparted a brownish or yellowish color to the interface. A few, small corundum plates were also associated with or oriented in the nephelite layer. A similar but slightly thinner and less uniform reaction rim was formed on semisiliceous pots.

Mullite needles and thin corundum plates occurred sparingly in glass-filled pores below the interface. The corundum plates were sometimes colored pale blue or violet-blue and were then pleochroic.

(c) FLINT GLASSES

(1) *F 5795 and F 605.*—A very thin, intermittent reaction rim consisted of isotropic cristobalite. No glass penetrated below the lining-glass interface.

(2) *F 617 and F 620.*—A double reaction rim was 0.1 to 0.2 mm in thickness on both lined and unlined pots. An irregular upper layer of skeletal cristobalite crystals (fig. 21) was partially intermixed with the lower layer of nephelite-kaliophilite solid solution and carnegieite-$\alpha KAlSiO_4$ solid-solution crystals (fig. 22). The lower layer usually contained traces of corundum and tiny inclusions of TiO_2, Fe_2O_3, or both oriented in the nephelite.

The alumina-rich lining was less resistant to attack by F 617 glass than the typical lining. Not only was a reaction rim, 0.1 to 0.2 mm

in thickness, formed at the interface, but penetration into and replacement of the lining occurred to a depth of 0.3 mm, especially along the walls of cracks. The reaction rim (fig. 23,A) had two parts: an upper layer of pine-tree cristobalite crystals and a lower layer of carnegieite-$\alpha KAlSiO_4$ solid-solution crystals. The penetration zone (fig. 23,B) also had two parts. Just below the reaction rim was a zone of nepheline-kaliophilite solid-solution crystals and numerous large corundum plates, which completely replaced the mullite and glassy bond of the refractory, but only partially replaced the aggregates of original corundum. Deepest within the lining was a zone of large corundum plates in glass which had replaced the mullite and glassy bond of the refractory but not the fine-grained corundum aggregates.

Pores in typical refractory penetrated by glass were slightly enlarged and a few continuous channels formed by corrosion. A small amount of mullite and corundum (fig. 24) occurred in deep yellow-colored glasses. These yellow glasses had indices of refraction (table 2) somewhat lower than those of the original glasses, while colorless glasses, which filled large cracks, had the approximate indices of refraction of the melts.

(3) *F 649.*—An even reaction rim was about 0.05 mm in width. This rim was a fine-grained mixture of isotropic $\alpha KAlSiO_4$ solid solution or $KAlSiO_4$ glass, nephelite-kaliophilite solid solution with minute inclusions, traces of skeletal cristobalite extending into the glass, and a few corundum plates at the base of the rim.

Mullite and corundum crystals and two glasses occurred below the interface as with F 617 and F 620 glasses.

(4) *F 720.*—The reaction rim, 0.1 to 0.15 mm in thickness, was a fine-grained mixture of isotropic and anisotropic grains and partly dissolved refractory material (fig. 25). The isotropic grains were, apparently, $KAlSiO_4$ glass. The anisotropic grains were of two kinds: crystals of kaliophilite and yellowish, irregular-shaped grains, some of which were TiO_2 or Fe_2O_3 inclusions, and others were, possibly, lead compounds.

Where glass penetrated below the interface, through cracks in the lining, pores were enlarged and some channels formed by corrosion. The bulk of the crystalline reaction material consisted of one or more lead-aluminum silicates (figs. 26, 27, and 28) of undetermined composition. Other reaction products included mullite needles, corundum plates, skeletal crystals of cristobalite, and tiny globules of metallic lead (fig. 27). The glass filling the small channels and containing the reaction crystals was deep yellow in color and had a low index of refraction (average about 1.64, minimum near 1.60). Large channels and cracks contained clear glass with the refractive index (1.720) of the original glass.

Abundant feathery (figs. 27 and 28) and prismatic (fig. 26) crystals had an average index of refraction of 1.61, moderate birefringence, and a large extinction angle. The X-ray diffraction pattern was similar to that of the crystals in preparation 128 [5] in the system PbO–Al_2O_3–SiO_2 [5]. This fact, together with lack of agreement of optical properties, suggests a new lead-aluminum silicate of undetermined composition. Some of the thicker, more tabular crystals had slightly

[5] The X-ray diffraction pattern of the present crystals contained all the lines of medium or greater intensity, except the first two, found in the pattern of preparation 128 [5].

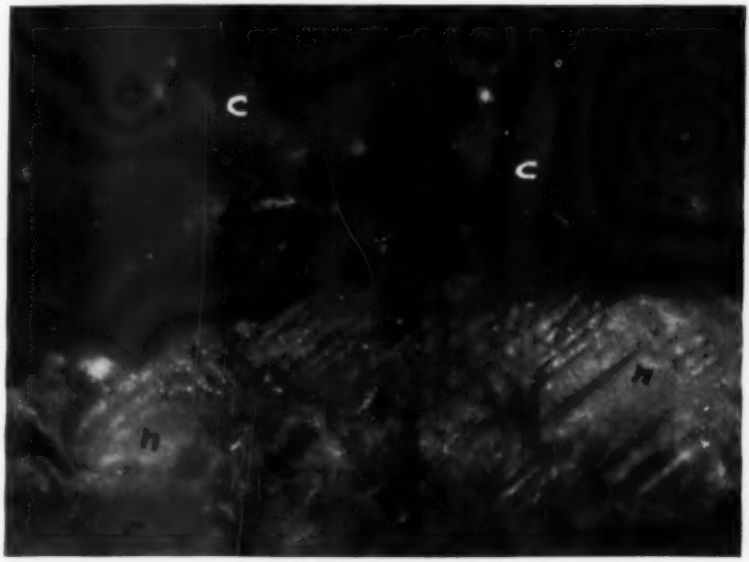

FIGURE 19.—*Refractory-glass interface of a BSC 517 melt.*

c, Intricately twinned carnegieite—$\alpha KAlSiO_4$ solid solution crystals; n, layer of twinned nephelite-kaliophilite solid solution crystals; r, refractory. Crossed nicols. Magnification × 520.

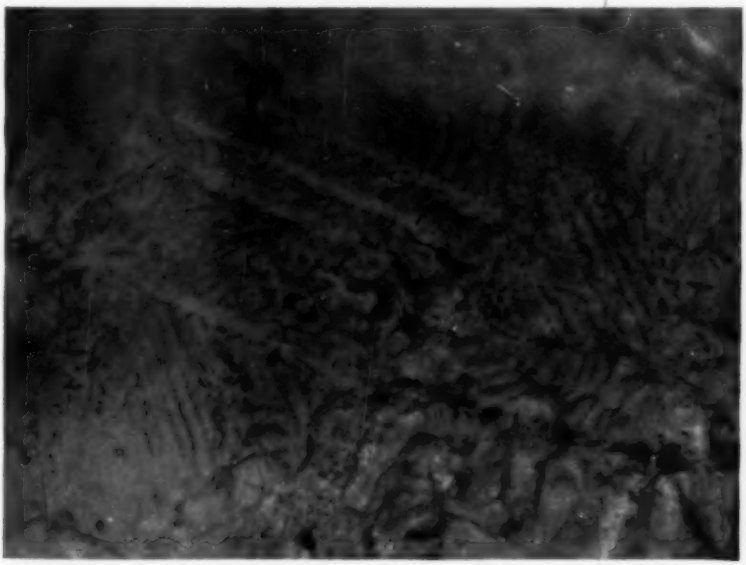

FIGURE 20.—*Oriented inclusions in nephelite-kaliophilite crystals at the refractory-glass interface of a BSC 511 melt.*

The small dark crystals and specks, apparently composed of TiO_2 or Fe_2O_3, or both, are arranged along twinning bands in the nephelite-kaliophilite solid solution crystals. Ordinary light. Magnification, × 520.

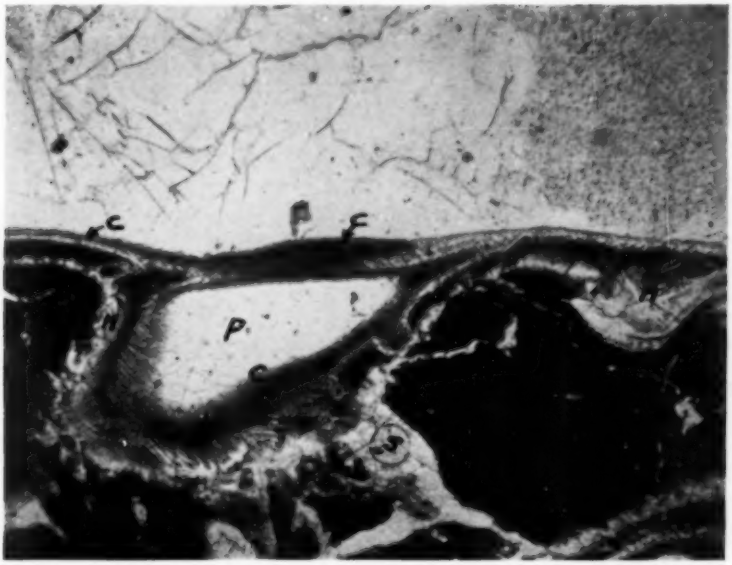

FIGURE 21.—*Refractory-glass interface of a F 617 melt.*

n, Layer of nephelite-kaliophilite and carnegieite—$\alpha KAlSiO_4$ solid solution crystals; c, cristobalite; p, a large pore in the refractory open to the melt except for a layer of reaction crystals; s, a small seed in glass. Black areas are refractory. Ordinary light. Magnification, × 46.

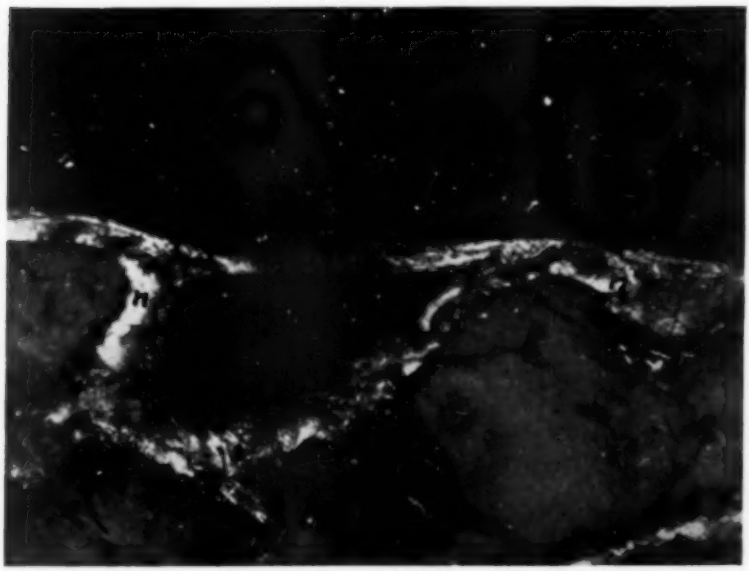

FIGURE 22.—*Same field as figure 21 but with crossed nicols.*

n, Doubly refracting nephelite-kaliophilite solid-solution crystals. Black areas are glass; cloudy, refractory material. Cristobalite is invisible. Magnification, × 46.

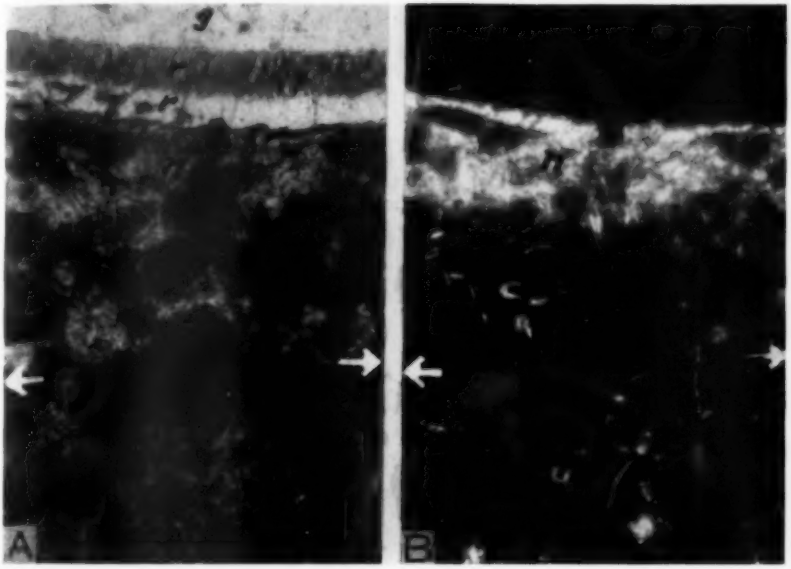

FIGURE 23.—*Alumina-rich lining penetrated by F 617 glass and lining-glass interface.*

A, Ordinary light; B, same field as A but with crossed nicols. Arrows indicate depth of glass attack. Black areas in A and gray clouded areas in B are the aggregates of corundum of the original lining (see fig. 6). g, Glass; r, reaction rim (invisible in B) at interface with cristobalite layer above and carnegieite—$\alpha KAlSiO_4$ layer below; n, nephelite-kaliophilite (light areas) partly replacing refractory; c, corundum plates (white lines) and glass (black) partly replacing refractory; u, unattacked refractory showing mullite (white areas) glassy bond (black), and corundum aggregates (gray). Magnification, × 180.

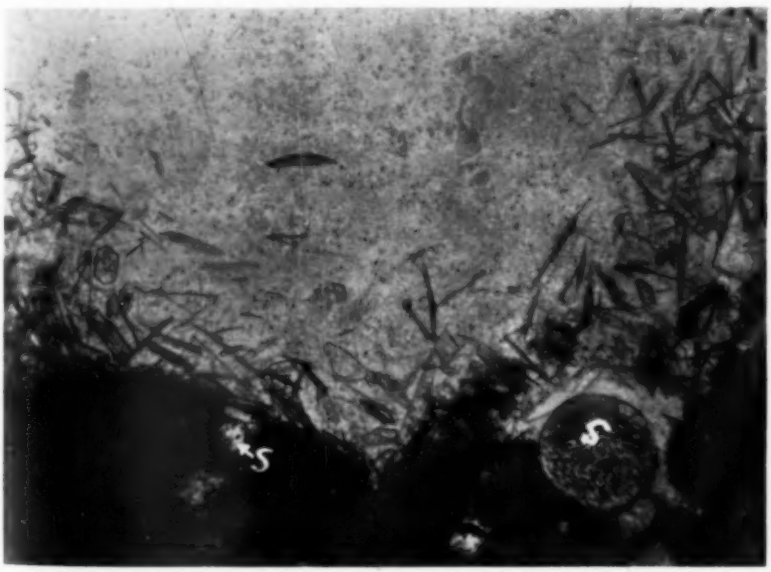

FIGURE 24.—*Corundum in pot bottom penetrated by F 617 glass.*

Corundum occurs in thin plates, many of which are standing on edge and look like needles or laths. Lightest areas are glass; darkest, refractory; s, seeds. Ordinary light. Magnification, × 120.

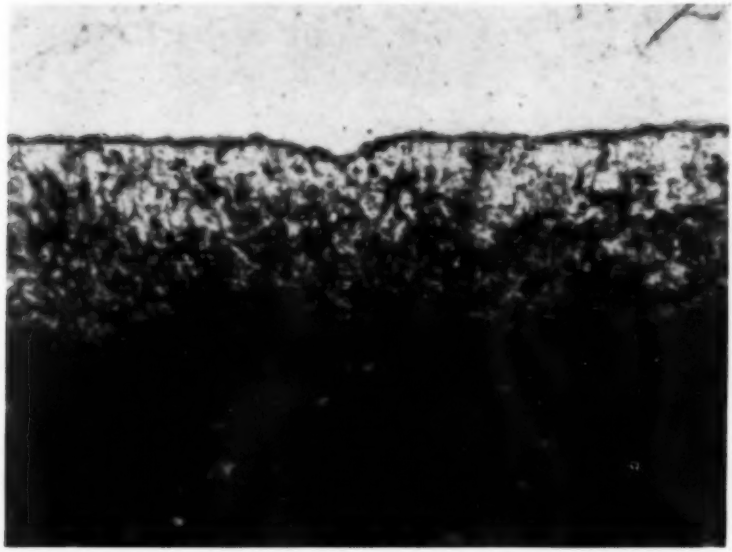

FIGURE 25.—*Lining-glass interface of a F 720 melt.*

Reaction zone (middle) of fine-grained $KAlSiO_4$ glass and nephelite (white grains) and various inclusions and undissolved remnants of the refractory (black grains). Melt above and unattacked refractory (black) below. Black line between melt and reaction zone is a refraction phenomenon. Ordinary light. Magnification, × 210.

FIGURE 26.—*Lead aluminum silicate in pot bottom penetrated by F 720 glass.*

p, Prismatic type of crystals; f, feathery type; r, refractory. Clear areas are glass. Ordinary light. Magnification, × 50.

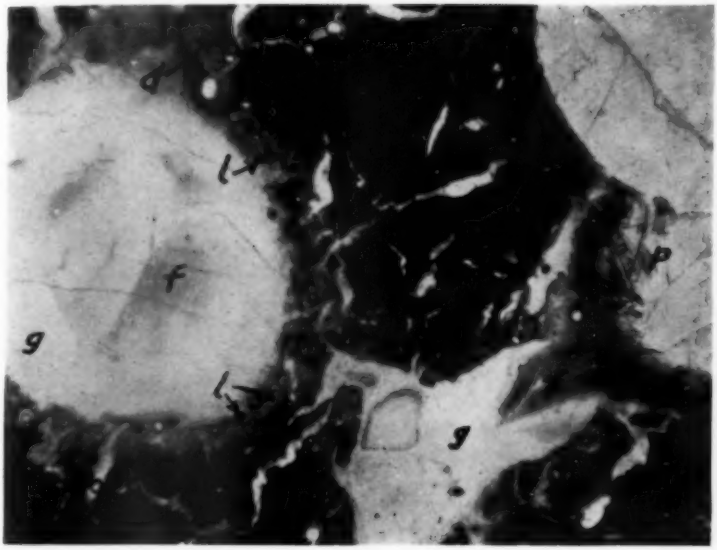

FIGURE 27.—*Reaction products in pot bottom penetrated by F 720 glass.*

p, Prismatic crystals of lead aluminum silicate; f, feathery crystals of lead aluminum silicate; l, globules of metallic lead; g, glass; d, partly dissolved refractory. Black areas are unattacked refractory. Ordinary light. Magnification, × 24.

FIGURE 28.—*Same field as figure 27 but with crossed nicols.*

White areas are doubly refracting crystals of lead aluminum silicate. Magnification, × 24.

lower birefringence and a higher index of refraction than the feathery crystals, suggesting the presence of more than one new lead-aluminum silicate.

VI. DISCUSSION

Layers of crystalline material (reaction rims) at the interface between both lined and unlined pots and any type of optical glass indicated that the refractory was attacked by the glasses. An approximate correlation was apparent between thickness and character of the rims and extent of corrosion and penetration of the pot bottoms by the glasses. For example, very thin or intermittent rims were found with glasses (LC 523, F 5795, and F 605) which did not corrode the pot, whereas thicker (0.1 to 0.2 mm) and sometimes multiple rims occurred with glasses which were moderately to extremely reactive.

The crystalline phases in the rims depended on the amount of refractory dissolved and the composition of the individual glasses. As indicated later, alumina and silica were the chief constituents dissolved from all types of refractory. Poorly defined rims of single oxides (corundum or cristobalite) were associated with glasses containing alkalies alone (17 percent in LC 523) or alkalies and a moderate amount of PbO (36 and 41 percent, respectively, in F 5795 and F 605) as the principal corrosive constituents. Thicker rims, composed largely of alkali-aluminum silicates (such as nephelite-kaliophilite solid solution) and cristobalite, occurred when the corrosive constituents included 8 to 12 percent of B_2O_3, 43 to 62 percent of PbO, or 13 to 20 percent of BaO, in addition to 4 to 23 percent of alkalies, as exemplified in the borosilicate crown and some flint and barium glasses. Rims of barium aluminum silicate (barium feldspar) and sometimes cristobalite, however, were associated with glasses containing 25 to 45 percent of BaO or BaO plus CaO. Lime, present in only one barium glass, apparently acted with BaO as a corrosive constituent and possibly formed a solid solution in the barium feldspar.

Multiple rims were indicative of considerable variation in composition in a very narrow zone (0.1 to 0.2 mm in thickness) at the pot-glass interface. In this zone the content of alumina increased on approaching the refractory, as shown by the order of the phases. For example, with many barium and lead glasses the phases were arranged (1) a layer of cristobalite, (2) an underlying layer of alkali or barium-aluminum silicates, and (3) an occasional concentration of corundum crystals with the lead glasses only. The corundum, however, was more often associated with nephelite, as described by Insley [6].

Glasses were classed as noncorrosive or corrosive, depending on the depth of penetration by the glass and the formation of enlarged pores and channels in the pot bottom. The crown and the flint glasses with 36 to 41 percent of PbO were classed noncorrosive because penetration, other than along cracks, was less than ½ in. and pores were not enlarged. Flint glasses with 43 to 51 percent of PbO were considered slightly corrosive because glass-filled pores were somewhat enlarged although penetration rarely extended more than ½ in. below the interface. A flint with 62 percent of PbO was a moderately corrosive glass, as indicated by occasional penetration to a depth of approximately 2 in., enlargement of pores, and formation of some channels by the glass. Most of the barium glasses were extremely corrosive, as shown by deep penetration, considerable enlargement of pores,

formation of extensive interconnecting channels, and occasional leakage in the melting furnace. Peddle [7 and 8] pointed out similar pot attack, indicated by corrosion extending nearly through the pot or by small holes in the center of the pot bottom, caused by glass with a BaO content of more than 40 percent and by glass with a high content of PbO.

The extent to which optical glass penetrated the pot bottom depended on many factors. Variations of the maximum temperature during the melting and fining operations of different glasses might be expected to have an effect on the extent of penetration [9 and 10]. No relation was apparent, however, partly because the actual temperature variations were not very great (1,350° to 1,450° C, with one exception at 1,200° C) and partly because any existing relations were masked by the effects of other factors.

The porosity of the refractory was one of the more important factors [11 and 12]. Penetration of glass into the bottoms of unlined pots was facilitated considerably by the elongated shape and vertical elongation of many pores. The linings, however, were not penetrated because the pores were fewer in number, much smaller, and essentially spherical in shape. Thus the underlying more porous refractory in the bottoms of lined pots was protected completely from penetration except when cracks or other flaws occurred in the lining.

In alumina-rich linings some of the batch constituents did not react, at the temperatures encountered in the preheating furances, to form a cohesive refractory with low porosity. Consequently, these linings were penetrated slightly by glass.

The viscosity of the molten glass was apparently sufficient to prevent penetration of the openings in the walls of the pot, especially toward the top, where the hydrostatic pressure of the melt was low. On the other hand, glass was sometimes forced into the pores in the bottom of the pot and the lower part of the walls, in spite of the viscosity, partly because of the increase in hydrostatic pressure. This would be especially true for the heavier glasses. For example, the flint glass (F 720) with the highest density penetrated the deepest of any flint. Unfortunately, the heavier glasses, F 720 and most barium glasses, were also extremely corrosive. These glasses were not only forced deep into the pot bottom but readily dissolved the refractory constituents exposed in the pore walls, enlarging and connecting the openings in the refractory to form winding and branching channels.

A wide variation in the resistance to glass attack of the different constituents of the refractory was apparent with the more corrosive glasses, although all glasses were at least mildly reactive. The crystalline phases were more resistant than the glassy bond. The portions of the refractory where mullite needles were most numerous, that is, the grains of potshell grog, were less subject to attack by the glass than regions in which glassy bond predominated. Hyslop [13] noted that between two otherwise similar pots the one with the higher mullite content was the more resistant to corrosion. The quartz and corundum in the special refractories, furthermore, were by far the most resistant of the constituents.

An explanation of the origin of the two types of glasses occurring in the refractory was suggested as a result of petrographic observations on the corroded regions of the refractory. When the walls of pores and channels were dissolved by molten barium or lead glasses,

the content of Al_2O_3 and SiO_2 in the attacking glass was increased. Thus, the resulting lowering of the refractive index of the altered glass can be accounted for because both vitreous silica and alumina have index factors below 1.46. Although the content of Fe_2O_3 and TiO_2 in the refractory was low, sufficient amounts of these oxides may have been dissolved to impart a yellow color to the relatively small amounts of altered glass in the openings of the refractory. By continued corrosion of the refractory, the altered glass gained access to additional pores and small channels. Unaltered glass from the melt was subsequently forced into some of the enlarged pores and channels pressing the altered glass against the channel walls and also deeper into the refractory. In this way a sharp division line was produced at the contact between the two glasses. Furthermore, the later unaltered glass apparently protected the melt from contamination with altered glass by isolating the latter in the pot bottom.

Crystalline reaction products in the altered glass depended on the amount and composition of the refractory dissolved as well as the composition of the melt [14 and 15]. Because SiO_2 and Al_2O_3 were the chief oxides dissolved from the refractory, the appearance of cristobalite, mullite, corundum, or some aluminate or silicate whose additional oxide constituent was derived from the glass was not surprising. In fact, the widespread formation of numerous needles of mullite, even with the noncorrosive glasses, was to be expected. Cristobalite, as suggested by its occurrence at the two glass contact, generally appeared where the content of dissolved Al_2O_3 was relatively low. Insley [6] has suggested that corundum, at the contact of clay refractories and soda-lime glass, was formed by the dissociation of aluminum silicates.

The occurrence of the aluminates and silicates was in accordance with known phase equilibrium relations. For example, zinc spinel ($ZnO.Al_2O_3$), which is the primary crystalline phase over a major part of the system SiO_2-ZnO-Al_2O_3 [16], was formed with all glasses that contained more than 2.5 percent of ZnO. Conversely, lead-aluminum silicates appeared only with the flint glass having the highest content of PbO (62 percent). Such silicates, however, should not be expected as reaction products except with glasses containing considerably more than 50 percent of PbO because the primary phase fields of the various known and suspected lead-aluminum silicates are limited to a small part of the entire field in the system PbO-Al_2O_3-SiO_2 [5]. That barium feldspar ($BaO.Al_2O_3.2SiO_2$) and barium disilicate were formed by glasses with a BaO content ranging from 13 to 45 percent suggested that these compounds have extensive fields in the system BaO-Al_2O_3-SiO_2.

The fact that seeds in the glass-filled channels in the pot bottom were largely associated with the altered glass throws some light on the origin and possible migration of the seeds. The formation of some of these seeds by molten glass entrapping the gas in the original pores was demonstrated by the great differences in the extent to which pores were filled with glass (section IV, p. 34). Other seeds probably were formed by the liberation of gases in the unfined molten glass. Seeds formed in either of the above ways would be more plentiful in the altered glass because the latter was not only the first glass to enter the pores of the refractory but entered, presumably, at an early stage in the fining period. That the altered glass was

isolated from the melt and that glass continued to move downward into the pot bottom apparently were arguments against migration of the seeds into the melt. The occurrence of very seedy glass in pots with badly cracked bottoms, however, suggested that some of these seeds possibly did migrate into the melt. Jebsen-Marwedel [17] believed that seeds he found originating in the refractory were released into the melt and suggested that the gas forming these seeds was a reaction product of pot attack.

VII. SUMMARY

Examinations were made visually and with a petrographic microscope of samples of pot bottom before and after the production of optical glass to determine the manner and extent of attack by the glass on the refractory and to identify the reaction products formed. In most instances, samples were selected that were cracked and penetrated by glass.

The refractory was composed of mullite needles in a glassy bond, both of which were attacked by the more corrosive glasses. Semisiliceous pots contained quartz grains and alumina-rich linings contained corundum crystals in addition to mullite and glass. The quartz and corundum were only slightly attacked, if at all, by molten glass.

The bottoms of unlined clay pots were penetrated sometimes by optical glasses, in large part because of the size, shape, and orientation of the pore spaces in the refractory. Lined pots, however, were not penetrated by any type of glass except when the relatively dense lining was cracked.

The corrosive action of barium glasses not only greatly enlarged but connected the pores in the refractory, forming a system of branching channels that sometimes continued entirely through the bottom. Crystalline reaction products identified at the interface between pot and glass (reaction rims) were barium feldspar, nephelite-kaliophilite solid solution and cristobalite. When glass penetrated the refractory barium feldspar, barium disilicate, zinc spinel, mullite and, occasionally, cristobalite and corundum were formed.

Borosilicate crown and most flint glasses were only slightly corrosive and did not noticeably enlarge the pore spaces nor form channel systems. The penetration of glass did not exceed about ½ in. A flint glass with 62 percent of PbO, however, was moderately corrosive. Nephelite-kaliophilite solid solution and related materials, cristobalite and corundum were found at the pot-glass interfaces. Mullite and corundum were the only reaction crystals in pot bottoms penetrated by these glasses, with the exception of the flint glass (F 720) with 62 percent of PbO. One or more new lead-aluminum silicates of undetermined composition and a trace of metallic lead occurred with this glass.

Variations of the maximum temperatures (1,350° to 1,450° C) in the glass-melting furnaces apparently did not affect the extent of penetration or the type or amount of reaction products formed.

The presence of two types of glasses was characteristic of refractory penetrated by barium and some lead glasses. One type was a glass altered in composition and certain physical properties by the attack on the pot constituents. This glass contained numerous seeds formed

by the entrapment of the gas in the original refractory and probably, also by the liberation of gas in the glass batch. The second type of glass resembled closely the melt.

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pH STANDARDS AT VARIOUS TEMPERATURES: AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

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ABSTRACT

pH values of aqueous solutions of acid potassium phthalate, National Bureau of Standards Standard Sample 84a, are given for concentrations from 0.001 to 0.2 *m* and for temperatures between 0° and 60° C. They were calculated from the values of the two dissociation constants of *o*-phthalic acid and the activity coefficients of the acid phthalate and phthalate ions. The pH values range from 3.88 to 4.42. They may be computed for any temperature from 0° to 60° C, inclusive, by the equation

$$pH = A^*/T + B + CT$$

or by the equation

$$pH = pH_{15} + k(t-15)^2$$

where A^*, B, C, and k are constants whose numerical values are dependent upon the molality of the solutions, pH_{15} is the pH value at 15° C, and $T = t°C + 273.16$.

A 0.05-*m* solution of acid potassium phthalate, the one used most extensively in the calibration of pH assemblies, has a pH value of 4.005 at 25° C. Its pH value at any temperature from 0° to 60° C, inclusive, may be computed by the equation

$$pH = 1336.08/T - 5.2678 + 0.016069T,$$

or by the equation

$$pH = 4.000 + 0.0000479\ (t-15)^2.$$

The pH values of a 0.05-*m* solution of acid potassium phthalate prepared with Standard Samples 84a and 84b were found to agree within 0.001 pH unit at the various temperatures.

Directions are included for preparations of the solutions on a molal and a molar scale of concentration. A critique of the method of evaluating the pH values and comparisons with older values reported for 0.05-*M* and 0.2-*M* solutions are given.

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I. INTRODUCTION

Values of the two dissociation constants of *o*-phthalic acid have been reported previously [1, 2] [1] for temperatures 0° to 60° C, inclusive. With their use, it is possible to calculate the hydrogen-ion concentration and the pH of solutions of acid potassium phthalate of different concentrations and to compare the values with those determined by a short method previously described [3].

The hydrogen-ion concentration, m_H, of an aqueous solution of acid potassium phthalate is represented by the equation

$$m_H^3+[a+(K_1f_{H_2Ph})/(f_Hf_{HPh})]m_H^2+[(K_1K_2f_{H_2Ph})/(f_H^2f_{Ph})]m_H-(aK_1K_2f_{H_2Ph})/(f_H^2f_{Ph})=0, \quad (1)$$

or by

$$m_H=\left(\frac{K_1K_2/(f_H^3f_{Ph})(a-m_H)}{K_1/(f_Hf_{HPh})+a+m_H}\right)^{1/2}, \quad (2)$$

with the reasonable assumption that the effects of hydrolysis are negligible. In these equations a is the stoichiometric concentration of the solution of acid potassium phthalate, K_1 and K_2 are, respectively, the first and second dissociation constants of *o*-phthalic acid, and f is the activity coefficient of the species denoted by subscripts.[2]

The hydrogen-ion activity, a_H, is given by [3]

$$a_H=f_Hm_H, \quad (3)$$

and the pH value by

$$pH=-\log a_H=-\log f_Hm_H. \quad (4)$$

The activity coefficients [1, 2] of the various ions in a solution of acid potassium phthalate with or without dipotassium phthalate, *o*-phthalic acid, or potassium chloride are given by the Hückel [6] form of the Debye-Hückel equation, or by [4]

$$-\log f_H=A\sqrt{\mu}/(1+3.76\ B\sqrt{\mu})-\beta_Hm_H, \quad (5)$$

$$-\log f_{Cl}=A\sqrt{\mu}/(1+3.76\ B\sqrt{\mu})-\beta_{Cl}m_{Cl}, \quad (6)$$

$$-\log f_{HPh}=A\sqrt{\mu}/(1+3.76\ B\sqrt{\mu}-\beta_{HPh}m_{HPh}, \quad (7)$$

and

$$-\log f_{Ph}=4A\sqrt{\mu}/(1+3.76\ B\sqrt{\mu})-\beta_{Ph}m_{Ph}. \quad (8)$$

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Equations 1, 2, 9, and 10 are based on the mass-action equations for the dissociation of o-phthalic acid, the equation $a=m_{H_2Ph}+m_{HPh}+m_{Ph}$, and the equation $a+m_H=m_{HPh}+2m_{Ph}$, expressing electrical neutrality of the solutions. Equation 12 is derived in a similar manner except the concentration of the hydroxyl ion, m_{OH}, is included, so that $a+m_H=m_{HPh}+2m_{Ph}+m_{OH}$. Acid potassium phthalate is considered to be completely dissociated into potassium and acid phthalate ions. For more details and references to earlier work, see references [1 to 3]. In equations 1 or 2, the symbols H_2Ph, HPh, and Ph designate, respectively, undissociated o-phthalic acid, acid phthalate ion, and diphthalate ion. For convenience, the charges on the ions are omitted throughout the paper.

[3] The activity coefficient of an individual ion cannot be determined by thermodynamics alone without assumption. In the work on pH standards at this Bureau the assumption is made that the activity coefficients of ions are given by the Hückel equation and that the "salting-out" terms of the chloride and hydrogen ions are equal. The parameters of the Hückel equation are determined from a study of the thermodynamic properties of mixtures of acid potassium phthalate, dipotassium phthalate, o-phthalic acid, and potassium chloride. For details in regard to this procedure, see references [1 to 5].

[4] The equation of Hückel was derived for the activity coefficient of a single salt. Hückel assumed that the dielectric constant, D, of a solution varied with the salt concentration according to the equation $D=D_0(1-\beta c_s)$, where D_0 is the dielectric constant of the solvent and β is a proportionality constant. In this paper and previous ones [1, 2] the assumption was made that the Hückel equation may also be applied to a solution containing a mixture of salts. This assumption leads to eq 5, 6, 7, and 8. Frequently, experimenters assumed that the salting-out term is proportional to the ionic strength of the solutions. When this assumption is made, it follows that solutions of a particular buffer mixture of different compositions but of the same ionic strength have the same pH value [1]. Hamer and Acree [1], however, have shown that solutions of a particular buffer mixture of different compositions and of the same ionic strength have different pH values.

The activity coefficient of the undissociated *o*-phthalic acid, H_2Ph, is assigned a value of unity, as is customary for neutral molecules. The data of Scatchard, Hamer, and Wood [7] show that this is not strictly true for concentrated solutions but is a very close approximation for most solutions below 0.2 *m*.[5]

It is the purpose of this paper to present values of the pH of NBS Standard Sample 84a of acid potassium phthalate of concentrations ranging from 0.001 to 0.2 *m* and for temperatures from 0° to 60° C, based upon the above equations and the values of K_1, K_2, β_{Cl}, β_{HPh}, and β_{Ph} given in former reports [1, 2]. Values of A and B at various temperatures for use in the above equations are given in a previous publication [5].[6] The ionic strength of the solutions is given by $(m_K+m_{HPh}+4m_{Ph}+m_H)/2$ and the values of the molalities of the acid phthalate and diphthalate ions by the equations

$$m_{HPh}=[(K_1 f_{H_2Ph})/(f_H f_{HPh})](a-m_H)/[2m_H+(K_1 f_{H_2Ph})/(f_H f_{HPh})] \quad (9)$$

and

$$m_{Ph}=[m_H(a-m_H)]/[2m_H+(K_1 f_{H_2Ph})/(f_H f_{HPh})], \quad (10)$$

where a represents the molality of acid potassium phthalate and the other terms have their usual significance. The value of m_K is equal to a, as acid potassium phthalate is completely dissociated into potassium and acid phthalate ions.

II. CALCULATION OF THE pH VALUES OF AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

The method of calculation of pH values is illustrated by the data given in table 1 for a 0.05-*m* solution of acid potassium phthalate at 25° C. First, the solution is considered to consist only of K^+ and HPh^- ions. The ionic strength is then equal to the molality. The hydrogen-ion concentration is calculated by eq 2, taking m_H as zero on the right side of the equation. This value of m_H is then used on the right side of eq 2 and a new value is determined for m_H. This procedure is repeated until consistent values of m_H are obtained. Generally only three approximations are required. Values of m_{HPh} and m_{Ph} are then obtained by eq 9 and 10, and a new value of the ionic

TABLE 1.—*Values of molecular and ionic species and ionic strength in moles per 1,000 g of water, and the* pH *for 0.05-m solution of acid potassium phthalate corresponding to the several steps in the arithmetical procedure of successive approximations*

	Assumed values	Number of successive approximations						
		I	II	III	IV	V	VI	VII
HAn^-	0.05				0.043657	0.043637	0.043637	0.043637
H^+	.0	0.00012068	0.00012039	0.00012039	.00012039	.00012213	.00012214	.00012214
$An^=$	.0				.0032315	.0032424	.0032423	.0032423
H_2An	.0				.0031111	.0031203	.0031202	.0031202
μ	.05				.053412	.053426	.053426	.053426
pH	7	4.008	4.009	4.009	4.009	4.005	4.005	4.005

[5] In this paper the symbol *m* is used to denote molality and the symbol *M* to denote molarity.

[6] These values have since been revised [8]. The use of the new values, however, will not change the values of pH given in this paper, as the older values of A and B [5] were employed consistently throughout this investigation in the determination of the dissociation constants [1, 2], the concentrations of the various ions, and the value of the standard potential of the silver-silver-chloride electrode [5].

strength is calculated by using the values of m_{HPh} and m_{Ph}. The various quantities are given in table 1 under the column designated as approximation IV. The new ionic strength is used to calculate a new m_H, which in turn is used to calculate new values of m_{HPh} and m_{Ph}, and so on until self-consistent values of m_H, m_{HPh}, and m_{Ph} are obtained. Data in table 1 show the results of approximations V, VI, and VII. Values obtained in approximations VI and VII agree; hence no further arithmetical computations are required. The pH value of 0.05-*m* solution of acid potassium phthalate prepared with NBS Standard

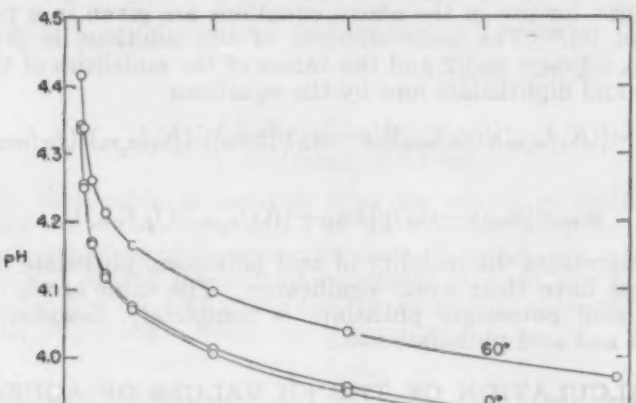

FIGURE 1.—*Plots of the* pH *values of aqueous solutions of acid potassium phthalate, National Bureau of Standards Standard Sample 84a, at 0°, 25°, and 60° C as a function of the molality of the solution.*

Sample 84a is therefore 4.005 at 25° C. The pH values of other concentrations at the various temperatures were determined in like fashion.

In table 2, values are given of m_H, m_{HPh}, m_{Ph}, and m_{H_2Ph} from 0° to 60° C for aqueous solutions of acid potassium phthalate from 0.001 to 0.2 *m*. The amount of m_{Ph} and m_{HPh} is larger for the more concentrated solutions than for the more dilute ones. On a percentage basis, however, the reverse is true because of the increased ionization of the acid phthalate ion on dilution.

The pH values of acid potassium phthalate from 0.001 to 0.2 *m* are given in table 3 for temperatures from 0° to 60° C, inclusive. In figure 1 the values are shown as a function of the molality of acid potassium phthalate at 0°, 25°, and 60° C. From 0.05 to 0.2 *m* the pH values do not change very much. The pH of any intermediate concentration can be interpolated from the data of table 3 or read from the curves of figure 1.

TABLE 2.—*Concentrations (molality×10⁴) of molecular and ionic species in solutions of acid potassium*

TABLE 2.—*Concentrations (molality×10⁴) of molecular and ionic species in solutions of acid potassium phthalate of various molalities at temperatures from 0° to 60° C*

Temperature	m=0.001 KHPh *				m=0.002 KHPh				m=0.005 KHPh				m=0.01 KHPh			
	H^+	HPh^-	$Ph^=$	H_2Ph	H^+	HPh^-	$Ph^=$	H_2Ph	H^+	HPh^-	$Ph^=$	H_2Ph	H^+	HPh^-	$Ph^=$	H_2Ph
°C																
0	0.4736	8.871	0.8013	0.3277	0.5848	17.83	1.377	0.7922	0.7276	44.59	3.069	2.341	0.8380	88.97	5.932	5.094
5	.4808	8.851	.8150	.3342	.5938	17.79	1.401	.8075	.7388	44.49	3.124	2.385	.8514	88.77	6.042	5.191
10	.4847	8.837	.8241	.3394	.5983	17.76	1.418	.8195	.7444	44.42	3.164	2.420	.8581	88.62	6.122	5.263
15	.4862	8.826	.8302	.3440	.5998	17.74	1.430	.8298	.7460	44.36	3.194	2.448	.8601	88.49	6.184	5.324
20	.4852	8.819	.8334	.3482	.5982	17.73	1.436	.8380	.7437	44.32	3.213	2.469	.8575	88.41	6.225	5.367
25	.4820	8.817	.8326	.3506	.5937	17.71	1.438	.8438	.7376	44.29	3.222	2.484	.8505	88.35	6.249	5.399
30	.4765	8.818	.8291	.3526	.5862	17.72	1.434	.8476	.7275	44.29	3.219	2.491	.8388	88.34	6.250	5.411
35	.4685	8.823	.8227	.3542	.5755	17.72	1.425	.8500	.7133	44.30	3.207	2.494	.8223	88.35	6.235	5.413
40	.4585	8.831	.8134	.3549	.5623	17.74	1.413	.8510	.6960	44.33	3.185	2.489	.8022	88.40	6.200	5.398
45	.4465	8.842	.8024	.3559	.5466	17.76	1.395	.8483	.6756	44.37	3.155	2.479	.7785	88.49	6.145	5.367
°C																
50	.4324	8.860	.7867	.3543	.5282	17.79	1.372	.8439	.6519	44.43	3.110	2.458	.7508	88.61	6.072	5.321
55	.4169	8.879	.7688	.3519	.5081	17.82	1.345	.8365	.6257	44.51	3.058	2.433	.7204	88.76	5.981	5.261
60	.4007	8.899	.7507	.3500	.4872	17.85	1.317	.8293	.5988	44.59	3.004	2.405	.6891	88.92	5.886	5.196

Temperature	m=0.02 KHPh				m=0.05 KHPh				m=0.1 KHPh				m=0.2 KHPh			
	H^+	HPh^-	$Ph^=$	H_2Ph	H^+	HPh^-	$Ph^=$	H_2Ph	H^+	HPh^-	$Ph^=$	H_2Ph	H^+	HPh^-	$Ph^=$	H_2Ph
°C																
0	0.9654	177.3	11.85	10.88	1.192	440.0	30.59	29.40	1.438	873.7	63.87	62.44	1.7748	1732.3	134.74	132.96
5	.9815	176.8	12.07	11.09	1.214	438.8	31.19	29.97	1.465	871.2	65.15	63.68	1.8114	1726.7	137.56	135.74
10	.9898	176.5	12.23	11.24	1.225	438.0	31.63	30.41	1.481	869.2	66.13	64.65	1.8334	1722.3	139.78	137.95
15	.9927	176.3	12.36	11.37	1.231	437.2	32.00	30.76	1.489	867.6	66.94	65.45	1.8466	1718.6	141.64	139.80
20	.9903	176.1	12.45	11.46	1.229	436.7	32.25	31.02	1.490	866.4	67.52	66.03	1.8494	1715.8	143.01	141.16
25	.9827	175.9	12.52	11.54	1.221	436.4	32.42	31.20	1.482	865.6	67.94	66.46	1.8432	1713.7	144.09	142.25
30	.9697	175.9	12.53	11.56	1.207	436.2	32.50	31.30	1.467	865.1	68.17	66.70	1.8269	1712.4	144.72	142.89
35	.9510	175.9	12.51	11.56	1.185	436.2	32.49	31.31	1.442	865.0	68.20	66.76	1.7997	1711.9	144.97	143.17
40	.9282	176.0	12.45	11.52	1.158	436.4	32.39	31.23	1.412	865.3	68.05	66.64	1.7649	1712.1	144.84	143.07
45	.9010	176.2	12.35	11.45	1.126	436.8	32.16	31.04	1.374	866.1	67.65	66.28	1.7207	1713.4	144.16	142.44
50	.8694	176.4	12.22	11.35	1.088	437.3	31.87	30.78	1.330	867.1	67.11	65.78	1.6680	1715.2	143.22	141.56
55	.8344	176.7	12.05	11.22	1.046	438.1	31.47	30.43	1.280	868.6	66.34	65.06	1.6089	1718.1	141.73	140.12
60	.7985	177.0	11.88	11.08	1.002	438.9	31.07	30.06	1.229	870.1	65.58	64.35	1.5476	1720.8	140.40	138.85

* KHPh denotes acid potassium phthalate.

TABLE 3.—pH *values of various molalities of acid potassium phthalate, Standard Sample 84a of the National Bureau of Standards, from 0° to 60° C*

Temperature	pH values							
	$m=0.001$	$m=0.002$	$m=0.005$	$m=0.01$	$m=0.02$	$m=0.05$	$m=0.1$	$m=0.2$
°C								
0	4.341	4.255	4.171	4.122	4.076	4.012	3.956	3.905
5	4.334	4.248	4.165	4.115	4.069	4.005	3.949	3.897
10	4.331	4.245	4.162	4.112	4.066	4.001	3.945	3.893
15	4.330	4.244	4.161	4.111	4.065	4.000	3.944	3.891
20	4.331	4.246	4.163	4.113	4.067	4.001	3.945	3.892
25	4.334	4.249	4.167	4.117	4.070	4.005	3.948	3.894
30	4.339	4.255	4.173	4.124	4.077	4.011	3.953	3.899
35	4.346	4.263	4.182	4.133	4.086	4.019	3.962	3.907
40	4.356	4.273	4.193	4.144	4.097	4.030	3.972	3.917
45	4.367	4.286	4.206	4.157	4.111	4.043	3.985	3.929
50	4.381	4.301	4.222	4.174	4.127	4.059	4.000	3.944
55	4.397	4.318	4.240	4.192	4.145	4.077	4.018	3.962
60	4.415	4.337	4.260	4.212	4.165	4.097	4.037	3.979

In figure 2 the pH values are plotted with respect to temperature in degrees centigrade. This variation, which is quite small, may be expressed by an equation similar to that used by Harned and Robinson [9] for the variation of dissociation constants with temperature, namely,

$$\mathrm{pH}=A^*/T+B+CT. \tag{11}$$

The numerical values of the constants A^*, B, and C were determined by the method of least squares, using the pH data of table 3. The numerical values of the constants are given in table 4 for the various molalities of acid potassium phthalate.

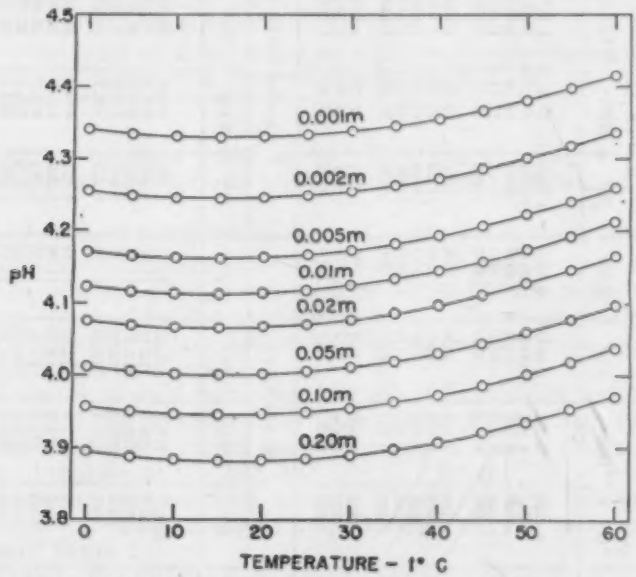

FIGURE 2.—*Plots of the* pH *values of aqueous solutions of acid potassium phthalate, National Bureau of Standards Standard Sample 84a, of various molalities as a function of the temperature in degrees centigrade.*

The variation of the pH values with temperature may also be expressed by the equation

$$pH = pH_{15} + k\,(t-15)^2, \qquad (11a)$$

where pH_{15} is the value for 15° C, and k is a constant whose numerical value depends on the stoichiometric concentration of acid potassium phthalate. The numerical values of the constant, k, are given in the last column of table 4 for various molalities of acid potassium phthalate.

TABLE 4.—*Numerical values of the constants of equations 11 and 11a for the variation of the* pH *values of various molalities of acid potassium phthalate with temperature*

Molality of acid potassium phthalate	A[a] (eq 11)	B (eq 11)	C (eq 11)	k (eq 11a)
0.001	1185.35	−3.8849	0.014230	0.0000423
.002	1251.83	−4.4517	.015099	.0000467
.005	1292.83	−4.8377	.015657	.0000491
.01	1321.45	−5.0867	.016003	.0000505
.02	1329.56	−5.1814	.016073	.0000503
.05	1336.08	−5.2678	.016069	.0000479
.10	1312.11	−5.1459	.015739	.0000464
.20	1312.12	−5.1824	.015648	.0000432

III. COMPARISONS OF THE pH VALUES WITH OLDER VALUES

In table 5 the values calculated for a 0.05-m solution are compared with ones obtained by previous investigators [3, 10, 11, 12, 13]. The values of Clark and Lubs are lower by 0.027 at 20° C than the ones reported in this paper, and those of Kolthoff and Tekelenburg are

TABLE 5.—*Comparison of the* pH *values of 0.05–m solution of acid potassium with values determined by different investigators*

Temperature	Clark and Lubs [10]	Kolthoff and Tekelenburg [11]	Hitchcock and Taylor [12]	MacInnes, Belcher, and Shedlovsky [13]	Hamer and Acree [3]	Present values	Δ[a]
t° C							
0					4.007	4.012	+0.005
5					4.002	4.005	+.003
10					3.999	4.001	+.002
12.5				4.000	4.000	[b] 4.000	±.000
15					4.000	4.000	+.000
18		3.94 [c](3.92)			4.001	[b] 4.000	−.001
20	3.974				4.003	4.001	−.002
25			4.008	4.000	4.008	4.005	−.003
30		3.96 (3.92)			4.016	4.011	−.005
35					4.025	4.019	−.006
38			4.023	4.015	4.032	[b] 4.027	−.005
40		3.99 (3.93)			4.036	4.030	−.006
45					4.050	4.043	−.007
50		4.02 (3.94)			4.068	4.059	−.009
55					4.084	4.077	−.007
60		4.05 (3.94)			4.101	4.097	−.004

[a] Differences between present values and former ones determined by Hamer and Acree [3].
[b] Values were calculated by equation 11.
[c] Values in parentheses were determined with a hydrogen electrode, whereas the other values of Kolthoff and Tekelenburg were determined with a quinhydrone electrode. They considered the hydrogen-electrode values less reliable because of possible reduction of the acid potassium phthalate.

lower by 0.06, 0.05, 0.04, 0.04, and 0.05, respectively, for temperatures of 18°, 30°, 40°, 50°, and 60° C. These differences may be attributed partially to the neglect of corrections for liquid-junction potentials and partially to their use of hydrogen-ion concentration rather than hydrogen-ion activity as the basis of the definition of the pH scale. Good agreement is obtained, however, with the results of Hitchcock and Taylor and of MacInnes, Belcher, and Shedlovsky.

The present values and those previously reported by Hamer and Acree [3] agree within 0.005, on the average, which is the limit of precision set by them. Hamer and Acree used a method in which a comparison was made of the emf of a cell containing 0.05–*m* acid potassium phthalate with the emf of two different cells, one containing 0.05–*m* hydrochloric acid and the other 0.05–*m* potassium hydroxide. Although the ionic strength of the hydrochloric acid and potassium hydroxide is 0.05, the ionic strength of acid potassium phthalate is somewhat higher, because of several ionic reactions that occur when the salt is dissolved in water. Hamer and Acree used an ionic strength of 0.0533 at each temperature. The true ionic strength may be calculated from the data of table 4. It is found to be 0.053378 at 25° C. Therefore, the value used for the ionic strength cannot account for the difference of 0.005 in pH cited above. Hamer and Acree used the activity coefficients of potassium hydroxide determined by Harned and Cook [14]. Harned and Cook determined the activity coefficients only for temperatures from 0° to 35° C, inclusive. Values of the activity coefficients of potassium hydroxide from 40° to 60° C were obtained by extrapolation of the data of Harned and Cook. The difference of 0.005 in pH, may, therefore, be attributed to the uncertainties in the values of the activity coefficients of potassium hydroxide, especially above 35° C.

The short method of Hamer and Acree, therefore, gives substantially the correct values of pH. This method also has added advantage in that it partially circumvents the theoretical difficulty of evaluating salting-out terms and "ion size" values of individual ions.

Clark and Lubs determined the pH of a 0.05-M solution of acid potassium phthalate by means of the cell

$$Pt, H_2(1\ atm)|KHPh(0.05\ M)|KCl(sat.)|KCl(0.1\ N)|Hg_2Cl_2|Hg.$$

They obtained 0.5689 v for the emf of this cell at 20° C. Using 0.3379 v for the 0.1-*N* calomel half-cell and neglecting the potential of the liquid junction between the saturated solution of potassium chloride and the phthalate solution, they obtained a pH value of 3.974. Recent data make possible a recalculation of the potential of the half-cell, including corrections for the potential of the liquid junction. MacInnes, Belcher, and Shedlovsky [13] obtained 0.3358 v and Hamer [15] found 0.3365 v for the 0.1-*N* calomel half-cell at 25° C. If the temperature coefficient of the 0.1-*N* calomel half-cell given by MacInnes [16] is used, the values of the potential of the half-cell become 0.3360 v and 0.3367 v, respectively, at 20° C. These potentials, together with the emf of Clark and Lubs give, respectively, 4.005 and 3.998 for the pH value at 20° C, or an average value of 3.999, which agrees well with 4.001 found in this investigation.[7]

[7] Clark and Lubs expressed their concentrations on a molar scale, whereas the concentrations used in this work were expressed on the molal scale. For concentrations below 0.2 *m*, differences in pH values introduced by differences in the concentration scale are negligible. A 0.05–*m* solution is 0.049646 *M*. (See table 7 for densities of KHPh.)

Kolthoff and Tekelenburg based their measurements upon Sorensen's [17] value of 2.038 for the pH of a solution composed of 0.01-*N* hydrochloric acid and 0.09-*N* potassium chloride at 18° C. This value was based upon conductivity measurements involving the Arrhenius isohydric principle. However, use of the activity concept alters this value. Harned and Hamer [18] obtained a value of 0.789 for the activity coefficient of 0.01-*m* hydrochloric acid in 0.09-*m* potassium chloride at 18° C, or 0.794 on a normal scale of concentration. As this solution has an activity of 0.00794, its pH value is 2.100 at 18° C. When used in conjunction with a salt bridge of saturated potassium chloride this solution should be assigned a pH value 0.02 pH unit lower, or a value of 2.080, because of the difference in the liquid-junction potentials of strong acids and weak buffers when used in contact with potassium chloride [15]. Hence, the values of Kolthoff and Tekelenburg become 3.98, 3.99, 4.00, 4.03, 4.05, and 4.08, respectively, for temperatures of 18°, 25°, 30° 40°, 50°, and 60° C, all of which agree fairly closely with the pH values given in this paper.

TABLE 6.—*Comparison of the* pH *values of 0.05-m solution of acid potassium phthalate at 25° C after corrections of literature data have been made*

Experimenters	Year	Uncorrected pH values	pH values	Estimated uncertainty *
Clark and Lubs	1916	3.974	4.003	0.01
Kolthoff and Tekelenburg	1927	3.95	3.99	.01
Hitchcock and Taylor	1937	4.008	4.008	.005
MacInnes, Belcher, and Shedlovsky	1938	4.000	4.000	.005
Hamer and Acree	1944	4.008	4.008	.005
Hamer, Pinching and Acree	1946	4.005	4.005	.002
Average value			4.004 ±0.005	0.006
Recommended value for National Bureau of Standards Standard Sample 84a or 84b, or Standard Samples of comparable purity.			4.005 ±0.002	0.002

* ±0.1 mv corresponds to ±0.0017 pH unit at 25° C.

In table 6 the various values, with corrections, for a 0.05-*m* solution of acid potassium phthalate are given for 25° C. The value of 4.005 obtained in this investigation agrees very well with the average value of 4.004. When it is realized that 0.1 mv in the emf corresponds to 0.0017 pH unit, the agreement is excellent. The differences between the two sets of values of MacInnes, Belcher, and Shedlovsky and of Hitchcock and Taylor correspond to 0.3 mv, which is an appreciable error for cells without liquid junction but not for cells with liquid junction, which they used in their determinations. The agreement of the pH values obtained in this investigation with those found by MacInnes, Belcher, and Shedlovsky, and by Hitchcock and Taylor, indicates that either pH method may be used. The method of MacInnes and Hitchcock is simpler and more direct, whereas the method herein described is more precise in that cells without liquid junction can be more accurately reproduced and lend themselves to thermodynamic treatment. Presumably, the different samples of acid potassium phthalate used by the various experimenters were of like purity and the various discrepancies may be attributed to the use of liquid junctions that are difficult to reproduce, to the use of

different types of hydrogen electrodes [19],[8] or to accidental errors. Nevertheless, the various values are in quite good agreement, and the pH value of a solution of acid potassium phthalate of a molality of 0.05 may be said to be established as 4.005 ±0.002 at 25° C.

Wood and Murdick [20] obtained 3.86 for the pH of a 0.2-*M* solution of acid potassium phthalate at 25° C from measurements with a saturated type of calomel half-cell, to which they assigned a value of 0.2437 v. Their pH value is 0.024 pH unit lower than the one obtained in this investigation. Recent data give 0.2434 v [15] and 0.2441 v [12] for the potential of the saturated calomel half-cell. The average value of 0.2438 v with the emf of Wood and Murdick gives 3.86 for the pH value. The difference of 0.024 between their value and the one reported here therefore must be due to either the difference in the pH methods, which becomes more pronounced at higher concentrations, or to the type of liquid junction used by Wood and Murdick.[9] The potential of a liquid junction between solutions of these types depends on the way it is constructed [15]. Unfortunately, no data are available for other concentrations with which comparisons may be made.

IV. PREPARATION OF THE pH STANDARDS OF ACID POTASSIUM PHTHALATE

Solutions of acid potassium phthalate of molalities from 0.001 to 0.2 are well suited for use as standards of pH. They possess good buffer capacities between 0.05 and 0.2 *m*, vary little in magnitude with changes in temperature, especially between 0° and 30° C, and may be readily prepared from a single salt and freshly boiled distilled water. It is recommended that they be prepared as follows: Add a known weight of dry acid potassium phthalate of high purity to 1,000 g of

TABLE 7.—*Quantities of acid potassium phthalate required to prepare solutions of various molalities.*[a]

Molality	Grams per 1000 grams of water	Density at 20° C	Density at 25° C	Grams per liter of solution	
				20° C	25° C
0.001	0.2042	0.99833	0.99716	0.2038	0.2036
.002	.4084	.99842	.99725	.4076	.4071
.005	1.0211	.99871	.99753	1.0187	1.0175
.01	2.0422	.99919	.99799	2.0364	2.0339
.02	4.0844	1.00014	.99892	4.0683	4.0633
.05	10.2109	1.00295	00171	10.1374	10.1249
.1	20.4216	1.00750	1.00616	20.1630	20.1362
.2	40.8432	1.01628	1.01484	39.8793	39.8228

[a] The weights given in the table are the weights of the substances in vacuum. International atomic weights of 1941 were used.

[8] Hamer and Acree [19] observed that hydrogen electrodes prepared with platinum or palladium sponge behave differently in solutions of acid potassium phthalate. They found that both types gave the same potential during the first 5 or 6 hours after the electrodes were immersed in the solutions. However, they found that the potentials of the electrodes prepared with platinum sponge constantly increased after 5 or 6 hours, whereas the potentials of the electrodes prepared with palladium sponge remained constant in many cases for well over 100 hours. The good agreement in the pH values of acid potassium phthalate reported by various experimenters and given above indicates that most of the measurements with hydrogen electrodes must have been made within a relatively short time.

[9] Wood and Murdick expressed their concentrations on a molar scale, whereas the concentrations used in this work are expressed on the molal scale. A 0.2-*m* solution corresponds to a 0.195-*M* solution (see table 7 for densities). Extrapolation to 0.2-*M* gives a pH of 3.881, which is 0.021 pH unit higher than the value of Wood and Murdick.

distilled water of pH 6.7 to 7.3. No preservative is necessary, and the solutions will keep in a glass-stoppered Pyrex bottle for at least 6 months with no change in pH. The requisite weights corrected to vacuum of acid potassium phthalate to be added to 1,000 g of water are given in the second column of table 7.

The purity (effective neutralizing power) of acid potassium phthalate may be determined by titrating a known weight of the salt with a standard solution of potassium hydroxide. Reagents and apparatus should be free of carbon dioxide or carbonates. The end point, which corresponds to a solution of dipotassium phthalate, may be determined by a pH meter or with a solution of phenolphthalein. The pH of solutions of dipotassium phthalate may be calculated by using values of K_1, K_2, β_{Ph}, β_{HPh}, and β_H given previously [1, 2] and eq 4, 5, 6, 7, and 8 and the eq

$$m_H^4+(K_1'+2a)m_H^3+(aK_1'+K_1'K_2'-K_w')m_H^2-$$
$$(K_w'K_1')m_H-K_w'K_1'K_2'=0 \quad (12)$$

giving the hydrogen-ion concentration of dipotassium phthalate. K_1', K_2', and K_w' refer, respectively, to $K_1 f_{H_2Ph}/f_H f_{HPh}$, $K_2 f_{HPh}/f_H f_{Ph}$, and $K_w a_{H_2O}/f_H f_{OH}$ where K_w is the dissociation constant of water [18], a_{H_2O} is the activity of water, f_{OH} is the activity coefficient of the hydroxyl ion, and the other terms have the same significance as given above. At 25° C, the pH values of solutions of dipotassium phthalate having molalities of 0.01, 0.04, 0.05, 0.06, and 0.10 are, respectively, 8.55, 8.74, 8.77, 8.79, and 8.83. The pH values of a 0.05-*m* solution are 8.94, 8.85, 8.77, 8.69, and 8.61, respectively, at temperatures of 15°, 20°, 25° 30°, and 35° C. Therefore, if about 1 g of acid potassium phthalate in 50 ml of distilled water is titrated with 0.1-*N* potassium hydroxide, the concentration of dipotassium phthalate at the end point will be approximately 0.05-*m* and the pH will be 8.8 at 25° C and 8.7 at 30° C. Frequently, sodium hydroxide is used as the titrant. In this case the solution at the end point will be sodium potassium phthalate, and the pH will be somewhat different than when potassium hydroxide is used as the titrant. Unfortunately, the values of the activity coefficients of the sodium salts of *o*-phthalic acid are not known. In general, however, the activity coefficients of sodium salts are higher than potassium salts. Therefore, it is to be expected that the pH of a solution of sodium potassium phthalate will be lower than that of a solution of dipotassium phthalate of equivalent concentration. Results given in the NBS certificate for Standard Sample 84c of acid potassium phthalate indicate that this is the case. A 0.05-*m* solution of sodium potassium phthalate has a pH value of 8.6 at 25° to 28° C.

In order that the solutions of acid potassium phthalate may be prepared on a volumetric basis, the densities of 0.02-, 0.05-, 0.10-, and 0.20-*m* solutions were determined at 20° and 25° C with the usual type of Ostwald picnometer of 50-ml capacity, using a tare of the same volume. Four independent determinations of the densities were made at each temperature. Average values are given in columns 3 and 4 of table 7. The data for solutions more dilute than 0.02-*m* were obtained from a smooth curve drawn through the densities of water and of solutions of higher concentrations. The requisite

weights of acid potassium phthalate for a liter of solution at 20° and 25° C are given in the last two columns of table 7.

For high accuracy, it is suggested that acid potassium phthalate, NBS Standard Sample 84a, having a certified purity of 100.00 percent, determined by titration, be used. It should be prepared for use as specified on the certificate. Standard Sample 84b may also be used. It has a purity of 100.04 percent, however. In order to ascertain if this small amount of acid impurity would appreciably affect the pH value of a 0.05-*m* solution, a series of measurements of the emf of hydrogen–silver-chloride cells without liquid junction were made with this sample. Experimental details have been described previously by Hamer and Acree [1, 2, 4]. Results are given in table 8 for measurements at 0°, 15°, 25°, 35°, 45°, and 60° C for solutions containing different amounts of potassium chloride. From these measurements, values of $-\log (f_H f_{Cl} m_H)$ were calculated for each concentration of potassium chloride by the method previously described [3]. In figure 3 the values are plotted as a function of the molality of potassium chloride. The values for Standard Sample 84a given in a former paper [3] are included for comparison. Extrapolation to zero concen-

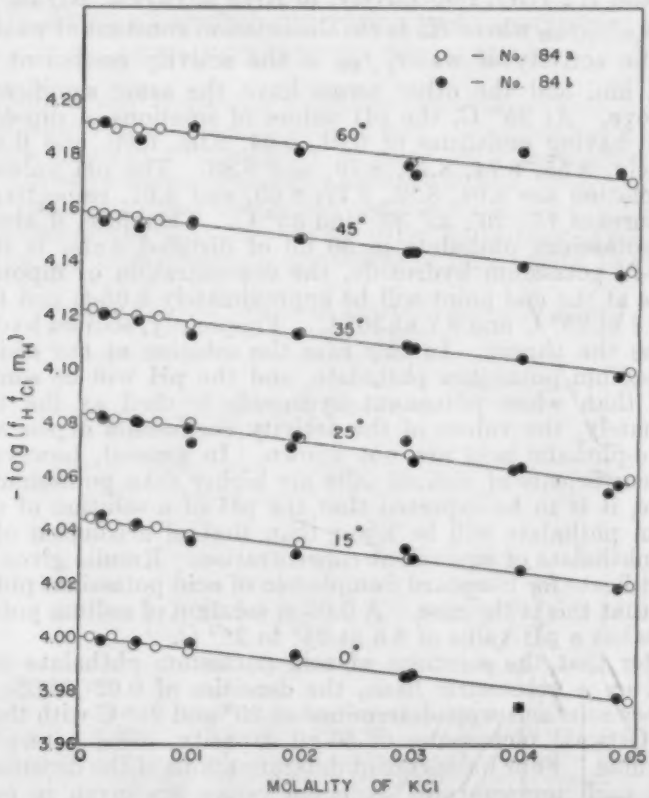

FIGURE 3.—*Plots of* $-\log (f_H f_{Cl} m_H)$ *as a function of the molality of potassium chloride for 0.05-m solutions of acid potassium phthalate, Standard Samples 84a and 84b issued by the National Bureau of Standards.*

tration of potassium chloride gives the values of $-\log (f_H f_{Cl} m_H)^\circ$ for a solution of acid potassium phthalate containing no chloride ion.

The pH value is then calculated from this value by means of the equation

$$pH=[-\log (f_H f_{Cl} m_H)^\circ - P]/Q, \quad (13)$$

the derivation and constants of which are given by Hamer and Acree [3]. Values of the pH for a 0.05-*m* solution of acid potassium phthalate, Standard Sample 84b, calculated by means of eq 13 are given at the bottom of table 8 for the various temperatures and are compared with the values for Standard Sample 84a [3]. The slight differences of 0.001 to 0.002 pH unit between solutions prepared with Standard Samples 84a and 84b are well within the experimental error of the two series of measurements. Consequently, either sample may be used in the preparation of a solution of acid potassium phthalate for use as a pH standard. It is to be expected that other Standard Samples of acid potassium phthalate having purities comparable with Standard Samples 84a and 84b will have pH values equal to those of Standard Samples 84a and 84b.[10]

TABLE 8.—*Electromotive forces of the galvanic cell* Pd, H_2 | (g) KHPh(0.05 *m*), | KCl(*m*) | AgCl(s) | Ag(s) *for acid potassium phthalate, NBS Standard Sample 84b*

Molality of potassium chloride	Temperature in degrees centigrade					
	0°	15°	25°	35°	45°	60°
	E	E	E	E	E	E
0.0020000	0.60422	0.61619	0.62403	0.63182	0.63952	0.65153
.005196	.58171	.59231	.59938	.60634	.61319	.62371
.01011	.56597	.57544	.58181	.58806	.59517	.60493
.01970	.55009	.55861	.56484	.57067	.57643	.58518
.02965	.54004	.54858	.55424	.55958	.56490	.57312
.03037	.53952	.54777	.55318	.55888	.56425	.57228
.04015	.53284	.54059	.54589	.55123	.55626	.56475
.04898	.52780	.53526	.54039	.54554	.55061	.55854
.005052			.60011			
.009816			.58290			
.02921			.55447			
.03945			.54669			
.04811			.54068			
pH values of 0.05-*m* acid potassium phthalate •						
Standard Sample 84a	4.007	4.000	4.008	4.025	4.050	4.101
Standard Sample 84b	4.007	4.001	4.009	4.025	4.049	4.099

• Calculated by the abbreviated method given in a previous report [3].

In order to ascertain the consistency of the pH values given in table 3 for use in the calibration of commercial pH meters, a pH meter was calibrated with 0.05-*m* solution of acid potassium phthalate which had a pH value of 4.01. The meter was then used to determine the pH value of other concentrations of acid potassium phthalate. All the measurements were made in a constant temperature room at

[10] Since this work was done, Standard Samples 84a and 84b have been superseded by equivalent Standard Samples, Standard Sample 84c and 185. A 0.05-*m* solution of acid potassium phthalate has been found to have the same pH value, whether it is prepared with Standard Samples 84a, 84b, 84c, or 185.

25° C. In table 9, the pertinent data are given. The agreement between the standard pH values given in table 3 and the values determined by the commercial pH meter is good except for the 0.10-*m* solution. The glass electrode gives a value which is 0.01 greater than the standard value. However, this is well within the limits of accuracy of a commercial pH meter [21].

TABLE 9.—*Comparison of* pH *values of acid potassium phthalate obtained with hydrogen and glass (commercial) electrodes*

Molality of acid potassium phthalate	pH (hydrogen electrode)	pH (glass electrode)[a]			
		No. 1	No. 2	No. 3	Average
0.005	4.167	4.17	4.17	4.17	4.17
.01	4.117	4.11	4.11	4.11	4.11
.02	4.070	4.07	4.07	4.07	4.07
.05	4.005	[b](4.01)	(4.01)	(4.01)	4.01
.10	3.948	3.97	3.95	3.97	3.96

[a] Measurements obtained with the commercial glass electrode were made by Elizabeth E. Sager and Alice S. Carr.
[b] Glass electrodes were calibrated with a solution of this strength.

V. A CRITIQUE OF THE METHOD USED IN THE EVALUATION OF THE pH OF AQUEOUS SOLUTIONS OF ACID POTASSIUM PHTHALATE

The pH values of acid potassium phthalate given in this report were calculated from the dissociation constants of *o*-phthalic acid and the activity coefficients of the H^+, HPh^+, and Ph^- ions determined from the emf of hydrogen—silver-chloride cells without liquid junction. In the determination of these quantities, mixtures of phthalates and chlorides were used. The activity coefficients of the various ions were determined by the method of least squares, using the relationship: $\beta\mu = -\beta_{Cl}m_{Cl} - \beta_{HPh}m_{HPh} + \beta_{Ph}m_{Ph}$, where β is the "salting-out" term of the Hückel equation [6], given in equations above, and determined experimentally from the emf. It was necessary to assume that $\beta_H = \beta_{Cl}$, or that the activity coefficients of the hydrogen and chloride ions were equal except for the salting-out term. Only mean activity coefficients are obtained from the emf equation. The equations of Debye and Hückel are used to evaluate activity coefficients of ions. If instead, mixtures of phthalates and bromides had been used with silver bromide electrodes or if mixtures of phthalates and sulfates had been used with mercury-mercurous sulfate electrodes, the individual β values would have been determined, respectively, by $\beta\mu = -\beta_{Br}m_{Br} - \beta_{HPh}m_{HPh} + \beta_{Ph}m_{Ph}$ and $\beta\mu = -\beta_{SO_4}m_{SO_4} - \beta_{HPh}m_{HPh} + \beta_{Ph}m_{Ph}$, and β_H would be assumed to be equal in each case to β_{Br} or β_{SO_4}. As the β terms are independent of each other, the pH value is the same for acid potassium phthalate in the absence of chloride, bromide, or sulfate ion, but not in their presence because of the differences in their salting-out terms. Therefore, the pH values of acid potassium phthalate presented in this paper do not depend upon the reference electrode used but do depend upon the assumption used in the evaluation of the hydrogen ion. However, as the molality of H^+ ions in

acid potassium phthalate is only about 0.0001, the term $\beta_H m_H$ contributes only a very small (negligible) fraction to the value of f_H as β is generally less than unity. It will not matter, therefore, whether β_H is assumed equal to β_{Cl}, β_{Br}, or β_{SO_4}.

Certain theoretical difficulties are encountered in the evaluation of the salting-out terms and ion sizes of individual ions as given above. Experimentally, only mean activity coefficients are obtained, and recourse was taken to the equations of Debye and Hückel to evaluate the activity coefficients of the individual ions. However, this procedure should give a very close approximation to the activity of ions in solutions, especially in dilute solutions ($<0.1m$). It does not imply that the activities of individual ions have been evaluated. Theoretical difficulties attendant on the evaluation of the salting-out terms and ion sizes of individual ions may be partially circumvented by using the short method of Hamer and Acree [3], which is independent of the Debye-Hückel theory. This method gives substantially the same pH values for solutions of acid potassium phthalate as the more involved method described in this paper. In the method of Hamer and Acree the activity coefficient of the hydrogen ion is taken equal to the mean activity coefficient of hydrochloric acid alone or in salt solutions.

It has been reported that observed activity coefficients of mixtures may be reproduced within 0.001 for ionic strengths as high as 0.5 if the assumption is made that $\beta_\mu = -\beta_{Cl} m_{Cl} - \beta_{HPh} m_{HPh} + \beta_{Ph} m_{Ph}$. An error of 0.001 in the activity coefficient of the hydrogen ion introduces an error of 0.0005 in pH. Hamer and Acree [4] have shown that probable uncertainties of 0.05 mv in the emf and the potential of the silver–silver-chloride electrode in its standard state, an error of 0.1 percent in the concentration, and the probable uncertainties in the natural constants for use in the emf equations given by Wensel [22] combine to give an uncertainty of 0.001 in pH values. Hence, with due consideration to possible accidental errors and to the assumptions made in evaluating the activity coefficient of the hydrogen ion, the pH values reported in this paper and previous ones in the series dealing with phthalate mixtures are considered to be accurate to 0.002 pH unit.

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EXTRACTION OF ALUMINA FROM CLAYS AND HIGH-SILICA BAUXITES

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ABSTRACT

Two processes for extracting alumina from low-grade ores are described, one applicable to both clays and high-silica bauxites, and the other only to bauxites. In the former process, a line-containing sinter is prepared and annealed by cooling it slowly through the range of 1,300° to 1,200° C. The annealed sinter dusts to a powder which requires no grinding. This material is extracted with a solution containing about 200 g of Na_2CO_3 and 150 g of NaCl/liter, and an extract is obtained in which the concentration of Al_2O_3 is 70 to 80 g/liter and that of SiO_2, 1 to 2 g/liter. By boiling the extract with a seed charge of synthetic sodalite, $3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2NaCl$, its silica content is reduced to 0.1 percent of the alumina content or less. Alumina, suitable for the manufacture of aluminum by electrolytic reduction, is precipitated by passing carbon dioxide into the desilicated solution. About 95 percent of the alumina in the clay is recovered by this method.

The other process developed in this investigation involves the extraction of alumina from high-silica bauxites with sodium hydroxide-sodium chloride solution and recovery of soda and alumina from the residues by a modified soda-lime-sinter method. Recoveries in excess of 90 percent of the alumina in high-silica bauxites are obtained.

In cyclical operation of each process, the spent solution from the alumina-precipitation step is used in the treatment of a fresh batch of material.

When the bauxites are extracted with solutions containing mixtures of sodium hydroxide and sodium carbonate, sodium sulfate, sodium bromide, or sodium nitrate, the quantities of silica present in the extracts are lower, the higher the concentration of the salt. This is caused by the formation and increased stabilization of slightly soluble compounds related to sodalite. Comparisons of the X-ray diffraction patterns of various sodalite type compounds are presented. By the extraction of bauxite with sodium hydroxide solution, in the absence of added salts, a relatively soluble hydrated nephelite, $Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$, is formed, which has a crystal structure different from that of sodalite.

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I. INTRODUCTION

The object of the investigations was to develop alkaline processes, of possible commercial application, for the extraction of alumina from clays and high-silica bauxites.

In the extraction of alumina from an ore as sodium aluminate there are three principal methods: (1) Direct extraction of the untreated ore with sodium hydroxide solution, as in the Bayer process. [1] [1]; (2) treatment of the ore to give a product containing solid sodium aluminate, which is extracted with water; and (3) treatment of the ore to give a product containing calcium aluminate, which can be decomposed with sodium carbonate.

The first part of this paper deals with the extraction of alumina from high-silica bauxites by a combination of methods (1) and (2). The remainder of the report is concerned with the extraction of alumina from clays and high-silica bauxites by method (3) used as a modified lime-sinter process. In the three methods developed at the National Bureau of Standards, the final disilication is effected by the formation of the very slighlty soluble compound sodalite, $3Na_2O.3Al_2O_3.6SiO_2.2NaCl$.

II. EXTRACTION OF ALUMINA FROM HIGH-SILICA BAUXITES WITH SODIUM HYDROXIDE-SALT SOLUTIONS

1. MATERIALS AND GENERAL PROCEDURE

Four bauxites of compositions given in table 1, ground to such fineness that 80 to 90 percent passed a No. 200 sieve, were chosen for extraction. Other materials used included sodium hydroxide, sodium carbonate, sodium sulfate, sodium bromide, sodium chloride, and sodium nitrate.

The procedure followed in most experiments involved boiling or autoclaving the finely ground bauxite with 100 to 400 ml of a sodium hydroxide solution containing various proportions of sodium salts.

[1] Figures in brackets indicate the literature references at the end of this paper.

The experiments at boiling temperatures were made in iron containers fitted with reflux condensers, and those at 150° C in a bomb-type autoclave having a capacity of 1 liter. After a heating period of 1 to 3 hours, the residues were separated from the solutions by filtration and repulped at boiling temperature with 100-ml portions of water. Each residue was then washed on the filter with 100 ml of hot water and the combined extracts and washes made up to 1 liter in volumetric flasks. Analyses for silica were made by dehydration with sulfuric acid of aliquots large enough to contain 5 to 10 g of alumina. Alumina was determined in the filtrates from the silica determinations. In some cases the approximate concentrations of sodium hydroxide and carbonate in the extracts were determined by titration of aliquots with standard acid.

TABLE 1.—*Composition of bauxites*

Oxide	Bauxite			
	A	B	C	D
	%	%	%	%
SiO_2	10.22	19.80	19.89	11.08
Al_2O_3	50.78	44.14	50.57	56.18
Fe_2O_3	7.92	9.61	1.26	1.18
TiO_2	2.17	2.05	2.52	2.39
CaO	0.05	----	0.02	0.03
MgO	.02	----	.01	.01
Loss on ignition	28.80	23.58	25.30	28.38
Total	99.96	99.18	99.57	99.25

Extractions of the bauxites were made on both a laboratory and small pilot-plant scale. The solid residues from the pilot-plant extractions were dried, analyzed, and further treated to recover the alumina and soda they contained. This treatment consisted in mixing the residues with calcium carbonate, heating to suitable temperatures, and extracting the ground products with water or various alkaline solutions.

Studies were made of the structures, as revealed by X-ray diffraction patterns, and of the compositions of the solid residues remaining after extraction of the bauxites with sodium hydroxide solution alone and when various sodium salts were present. Synthetic preparations consisting of the various sodium salts were also investigated and compared with the residues from the extractions of the bauxites.

2. PRELIMINARY EXPERIMENTS

Because of an extensive background of research in this laboratory on the preparation and properties of the calcium aluminates and silicates [2], it was decided to investigate the recovery of alumina from various calcium aluminates. For this purpose quantities of $3\,CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, and isometric hydrated tricalcium aluminate, $3CaO.Al_2O_3.6H_2O$, prepared by the usual methods [3], were available. The preparations were ground to pass a No. 200 sieve, and 2-g samples were extracted for 2 hours with 100-ml portions of a solution containing 50 g of Na_2CO_3 per liter. The results of extractions of alumina at 25° C, 50° C, 85° C, and at boiling are given

in table 2. In making the extractions, mechanical stirring was employed at temperatures below boiling.

Because the hydrated calcium aluminate gave an appreciably better extraction than any of the anhydrous compounds, the possibility suggested itself of forming $3CaO.Al_2O_3.6H_2O$ from a mixture of bauxite and lime, for the purpose of subsequent extraction with sodium carbonate solution.

TABLE 2.—*Extraction of alumina from calcium aluminates*

[Extraction for 2 hours of 2-g samples, ground to pass No. 200 sieve, with 100 ml of sodium carbonate solution containing 5-g of Na_2CO_3. Mechanical stirring was used at temperatures below boiling]

Experiment	Temperature	Recovery of Al_2O_3 from—			
		$3CaO.Al_2O_3$	$5CaO.3Al_2O_3$	$CaO.Al_2O_3$	$3CaO.Al_2O_3.6H_2O$
1	25° C	33.8	66.1	84.6	89.4
2	50° C	27.5	77.2	92.2	94.3
3	85° C	28.7	72.9	95.5	96.6
4	Boiling	46.4	82.2	95.6	96.3

Accordingly, a slurry of bauxite and calcium hydroxide (molar ratio of CaO to Al_2O_3 in bauxite=3) was prepared and placed in an autoclave which was maintained at 150° C for 4 hours, with shaking at half-hour intervals. The product was removed, dried at 110° C, and examined microscopically. All the gibbsite originally in the bauxite had been converted to well-developed crystals of $3CaO.Al_2O_3.6H_2O$.

This product was boiled for 3 hours with 200 ml of a 20-percent Na_2CO_3 solution and filtered (experiment 1, table 3). Similar extractions with 20- and 30-percent Na_2CO_3 solutions were made of mixtures of the same quantities of $Ca(OH)_2$ and bauxite that had not been previously autoclaved. Sodium hydroxide extractions were also made of the bauxite with no added $Ca(OH)_2$. In all the experiments the quantity of material treated was equivalent to 58 g of bauxite per liter of solution.

TABLE 3.—*Recovery of alumina from bauxite A under various conditions*

The quantity of material extracted was equivalent to 58 g of bauxite A (29.5 g of Al_2O_3) per liter of solution. The extraction mixtures were boiled for 3 hr before filtering]

Experiment	Mix	Molar ratio CaO/Al_2O_3 in mix	Autoclave treatment of mix prior to extraction	Composition of extracting solution		Recovery of Al_2O_3	$\frac{SiO_2}{Al_2O_3}\times 100$ in extracted solution
				Na_2CO_3	NaOH		
				g/liter	*g/liter*	%	
1	Lime+bauxite	3	4 hr at 150° C	200	0	81	0.58
2	do	3	None	200	0	81	.32
3	do	3	do	300	0	71	.20
4	Bauxite only	0	do	0	74	77	1.29
5	do	0	do	0	200	81	1.33
6	do	0	do	0	300	83	1.44

Comparison of experiments 1 and 2, table 3, shows that there is no advantage in forming the tricalcium aluminate hydrate by preliminary autoclaving of the lime-bauxite mixture. It may be noted that there was less silica in the extracts in experiments 1 to 3 than in 4 to 6. In the first three experiments sufficient lime was present to convert

100 g of Na_2CO_3 per liter to 74 g of NaOH per liter on complete causticization, leaving 100 g of Na_2CO_3 per liter in excess in experiments 1 and 2, and 200 g of Na_2CO_3 per liter in excess in experiment 3. It appears that an increase in Na_2CO_3 is accompanied by a decrease in the concentration of silica in the extracts. This observation is in agreement with a statement by Pesin and Lileev [4] that sodium aluminate solutions can be desilicated by heating them in the presence of high concentrations of sodium carbonate.

Two series of extractions were made of bauxites B, C, and D with solutions containing mixtures of Na_2CO_3 and NaOH (tables 4 and 5). The purpose of the first series was to determine the molar ratios of the Na_2O (added as NaOH)[2] in the solution to the Al_2O_3 in the bauxites, that would dissolve the maximum quantities of alumina at the boiling temperatures of the solutions. In these experiments the volume of the extracting solution was 200 ml.

TABLE 4.—*Determination of optimum molar ratios of* Na_2O *(as* NaOH*) in extracting solution to* Al_2O_3 *in bauxites* [a]

Experiment	Bauxite designation	Quantity of bauxite used	Composition of solutions						Al_2O_3 extracted [b]
			Initial			Final			
			Na_2CO_3	NaOH	Molar ratio Na_2O (as NaOH): Al_2O_3 in bauxite	Na_2CO_3	NaOH	Al_2O_3	
		g/liter	*g/liter*	*g/liter*		*g/liter*	*g/liter*	*g/liter*	%
1	B	289	300	100	1.0	256.5	84.5	39.3	31
2	B	241	300	100	1.2	263.0	94.5	47.3	44
3	B	144	300	100	2.0	278.0	88.5	39.9	63
4	B	96.5	300	100	3.0	286.8	88.5	26.8	63
5	C	252.5	300	100	1.0	259.5	86.5	52.7	41
6	C	168	300	100	1.5	278.0	77.0	55.8	66
7	C	126	300	100	2.0	278.0	88.5	42.3	66
8	C	84	300	100	3.0	267.5	94.5	28.9	68
9	D	284	250	125	1.0	231.5	114.0	64.1	40
10	D	189.5	250	125	1.5	221.0	121.5	81.3	76
11	D	142	250	125	2.0	234.0	117.0	61.1	77
12	D	94.5	250	125	3.0	229.5	120.5	41.8	79

[a] Extracted by boiling for 3 hr.
[b] Based on original volume of extracting solution (200 ml).

Figure 1 shows the relationships between the percentages of Al_2O_3 dissolved from the bauxites and the molar ratios of Na_2O in the initial solutions to Al_2O_3 in the bauxites. It is evident that, at boiling temperatures, only very slight increases in the extraction of Al_2O_3 occur at molar ratios above 2.0.

It should be noted (table 4) that the concentrations of both Na_2CO_3 and NaOH remaining in solution are less than those initially present. This indicates that the solid residues must contain carbonate as well as Na_2O derived from both NaOH and Na_2CO_3.

A second series of extractions of the bauxites was made, both at boiling temperatures and 150° C, with solutions containing 125 g of NaOH per liter and various amounts of Na_2CO_3 as shown in table 5.

[2] Here and subsequently in the text, in the tables, and in figure 1, the designation Na_2O is intended to indicate the sodium hydroxide added to the mixtures as such, and does not include sodium hydroxide that may be formed by the partial hydrolysis of sodium carbonate.

The actual volume of the solutions used in the experiments was 400 ml, and the quantities of bauxite were such that the molar ratio of Na_2O (as NaOH) in the initial solutions to Al_2O_3 in the bauxites was 2.0. As before, the concentrations of Al_2O_3 and SiO_2 in the extracts are calculated on the basis of the original volume of the solutions and expressed in grams per liter.

The concentration of SiO_2 in the extracts is shown (in table 5) to decrease with increase in the Na_2CO_3 in the solutions, thus confirming

TABLE 5.—*Extractions of bauxites with solutions containing 125 g of sodium hydroxide per liter and various amounts of sodium carbonate*[a]

Experiment	Bauxite designation	Quantity of bauxite used	Na_2CO_3 in extracting solution	Temperature	Al_2O_3 in solution	SiO_2 in solution	Extraction of Al_2O_3 [b]	$\frac{SiO_2}{Al_2O_3}\times 100$ in solution
		g/liter	g/liter		g/liter	g/liter	%	
1	B	180	0	Boiling	50.2	0.228	63.2	0.45
2	B	180	125	do	42.1	.102	53.0	.24
3	B	180	250	do	48.6	.089	61.1	.18
4	B	180	375	do	48.0	.075	60.3	.16
5	B	180	0	150° C	48.8	.172	61.5	.35
6	B	180	250	150° C	50.1	.056	63.1	.12
7	C	157.5	0	Boiling	54.0	.324	67.9	.60
8	C	157.5	62.5	do	53.7	.177	67.5	.33
9	C	157.5	125	do	52.5	.147	66.0	.28
10	C	157.5	250	do	55.5	.130	69.8	.24
11	C	157.5	312.5	do	53.7	.129	67.5	.24
12	C	157.5	0	150° C	51.6	.146	64.9	.28
13	C	157.5	250	150° C	53.1	.074	66.8	.14
14	D	142	0	Boiling	61.8	.340	77.4	.55
15	D	142	62.5	do	61.3	.245	76.8	.41
16	D	142	125	do	61.4	.233	77.0	.38
17	D	142	250	do	61.8	.212	77.4	.34
18	D	142	0	150° C	61.3	.215	77.0	.35
19	D	142	250	150° C	60.6	.088	75.9	.14

[a] Extracted by heating for 3 hr.
[b] Based on original volume of extracting solution (400 ml).

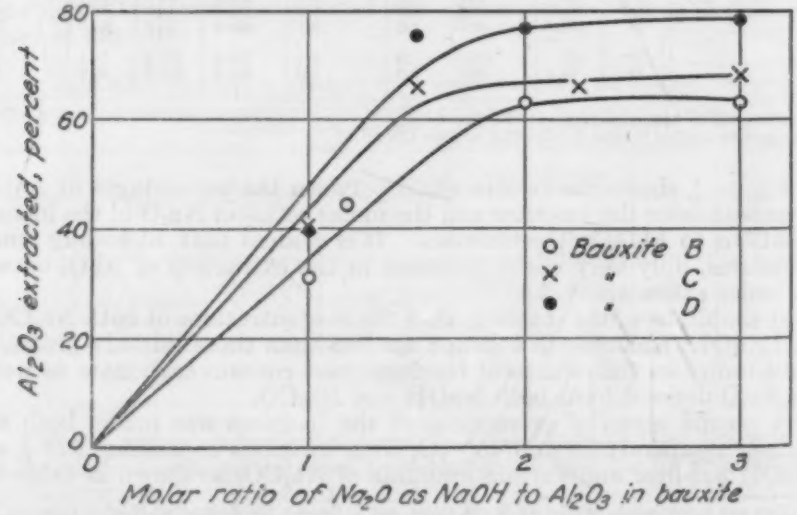
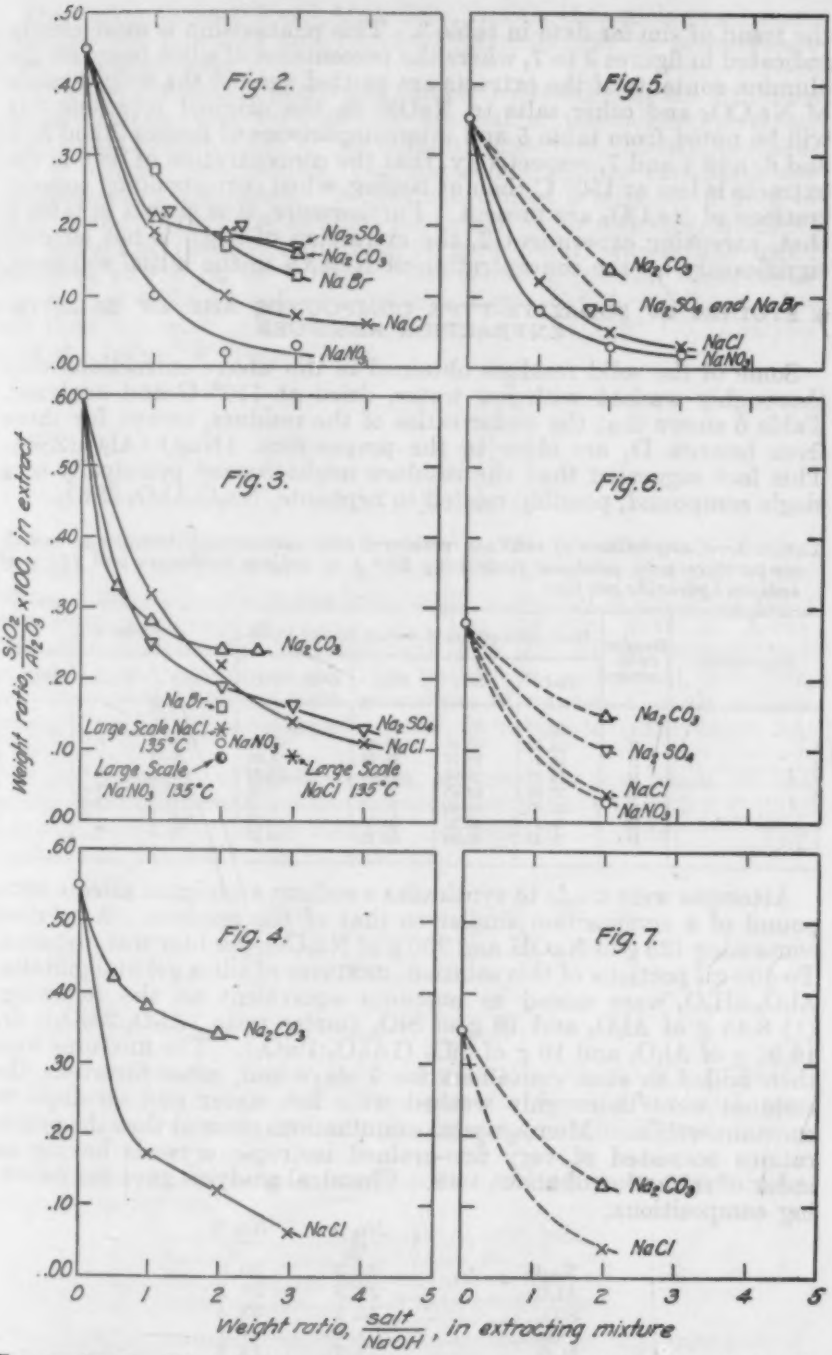


FIGURE 1.—*Effect of varying the molar ratio of* Na_2O *(as* NaOH*) in the extracting solutions to* Al_2O_3 *in the bauxites.*

Mixtures boiled or 3 hr.



FIGURES 2 to 7.—*Effect of sodium salts on the silica-alumina ratio in sodium hydroxide extractions from high-silica bauxites.*

Molar ratio of Na_2O (as NaOH) to Al_2O_3 in bauxite=2.0. Figures 2, 3, and 4, mixtures boiled for 3 hr; figures 5, 6, and 7, mixtures autoclaved at 150° C for 3 hr; figures 2 and 5, bauxite B; figures 3 and 6, bauxite C; figures 4 and 7, bauxite D. Points marked "Large Scale" represent data obtained in small-pilot-plant extractions at 135° C.

the trend of similar data in table 3. This relationship is more clearly indicated in figures 2 to 7, where the percentages of silica based on the alumina contents of the extracts are plotted against the weight ratios of Na_2CO_3 and other salts to NaOH in the original solutions. It will be noted from table 5 and intercomparisons of figures 2 and 5, 3 and 6, and 4 and 7, respectively, that the concentration of SiO_2 in the extracts is less at 150° C than at boiling, when corresponding concentrations of Na_2CO_3 are present. Furthermore, it is shown in table 5 that, excepting experiment 2, the extraction of Al_2O_3 is not affected significantly by the concentration of Na_2CO_3 in the initial solutions.

3. STUDIES OF SODALITE-TYPE COMPOUNDS AND OF BAUXITE-EXTRACTION RESIDUES

Some of the solid residues obtained in the above extractions were thoroughly washed with hot water, dried at 110° C and analyzed. Table 6 shows that the molar ratios of the residues, except for those from bauxite D, are close to the proportions, $1Na_2O:1Al_2O_3:2SiO_2$. This fact suggested that the residues might consist principally of a single compound, possibly related to nephelite, $Na_2O.Al_2O_3.2SiO_2$.

TABLE 6.—*Compositions of residues remaining after extraction of bauxites at boiling temperature with solutions containing 250 g of sodium carbonate and 125 g of sodium hydroxide per liter*

Experiment	Bauxite designation	Oxide composition of residue (ignited basis)				Molar ratio		
		Na_2O	Al_2O_3	SiO_2	$Fe_2O_3+TiO_2$	Na_2O	Al_2O_3	SiO_2
		%	%	%	%			
1	B	15.60	30.80	33.47	19.55	0.8	1.0	1.8
2	B	16.41	29.97	33.94	19.26	.9	1.0	1.9
3	B	16.32	29.96	34.00	19.04	.9	1.0	1.9
4	C	23.62	32.36	36.04	7.98	1.15	1.0	1.9
5	C	21.55	34.40	35.74	6.52	1.0	1.0	1.8
6	D	18.11	42.26	30.88	8.60	0.7	1.0	1.2
7	D	16.41	40.04	33.18	10.27	.7	1.0	1.4

Attempts were made to synthesize a sodium aluminum silicate compound of a composition similar to that of the residues. A solution containing 125 g of NaOH and 250 g of Na_2CO_3 per liter was prepared. To 400-ml portions of this solution, mixtures of silica gel and gibbsite, $Al_2O_3.3H_2O$, were added in amounts equivalent to the following: (1) 8.45 g of Al_2O_3 and 10 g of SiO_2 (molar ratio $1Al_2O_3:2SiO_2$); (2) 16.90 g of Al_2O_3 and 10 g of SiO_2 ($1Al_2O_3:1SiO_2$). The mixtures were then boiled in steel containers for 7 days and, after filtration, the residues were thoroughly washed with hot water and air-dried to constant weight. Microscopical examinations showed that the preparations consisted of very fine-grained isotropic crystals having an index of refraction of about 1.48. Chemical analyses gave the following compositions:

	No. 1	No. 2
	%	%
Na_2O	20.3	20.9
Al_2O_3	29.8	31.2
SiO_2	35.1	33.5
CO_2	1.8	1.1
H_2O	12.7	13.8
Fe_2O_3	0.1	0.0
Total	99.8	100.5

The corresponding Na_2O:Al_2O_3:SiO_2:Na_2CO_3:H_2O molar ratios are 0.98:1.00:2.00:0.14:2.42 and 1.02:1.00:1.82:0.09:2.50 for preparations 1 and 2, respectively.

An X-ray diffraction pattern of sample 1 showed that the structure of the crystals was very similar to that of the mineral sodalite, $3Na_2O.3Al_2O_3.6SiO_2.2NaCl$. A sodium aluminum silicate preparation of similar composition (but containing neither carbonate nor chloride) was synthesized. In this experiment a mixture of 26 g of gibbsite and 20 g of SiO_2, as silica gel (in the molar ratio $1Al_2O_3:2SiO_2$) and 600 ml of solution containing 90 g of NaOH was heated in an autoclave at 150° C for 5 days. The resulting product was filtered and washed with a small amount of hot water, followed by alcohol and then by ether. It was dried overnight at 110° C. Analysis gave the following composition:

	%
Na_2O	21.97
Al_2O_3	30.74
SiO_2	35.54
H_2O	11.46
Total	99.71

The corresponding molar ratios are $1.17Na_2O:1.00Al_2O_3:1.96SiO_2:2.11H_2O$. These ratios are in agreement with the composition of the hydrated nephelite, which has been reported formed in the desilication of sodium aluminate solutions [5]. The material gave an X-ray diffraction pattern distinctly different from that of the preparations containing sodium carbonate. Its pattern was identical, however, with that of the residue from extraction of bauxite C with sodium hydroxide solution containing no added carbonate (experiment 25, table 7).

In continuation of these studies, an analysis was made of the residue from a laboratory-scale extraction of bauxite C with a sodium hydroxide-sodium chloride solution (experiment 33, table 7). This residue had the following composition:

	%
Na_2O	22.46
Al_2O_3	32.75
SiO_2	33.46
$Fe_2O_3+TiO_2$	5.80
Cl	5.28
Total	99.75

The corresponding molar ratios are $0.90Na_2O:1.00Al_2O_3:1.74SiO_2:0.46NaCl$. The X-ray diffraction pattern of this material was identical with that given by a sample of natural sodalite obtained from Canada.

Four minerals have been recognized as belonging to the sodalite group [6], as follows:

Sodalite	$3Na_2O.3Al_2O_3.6SiO_2.2NaCl$
Noselite	$3Na_2O.3Al_2O_3.6SiO_2.Na_2SO_4$
Hauynite	$3Na_2O.3Al_2O_3.6SiO_2.2CaSO_4$
Lazurite	$3Na_2O.3Al_2O_3.6SiO_2.2Na_2S$.

In a further investigation of sodalite-type compounds, mixtures of 26 g of gibbsite and 20 g of SiO_2 as silica gel (in the molar ratio $1Al_2O_3:2SiO_2$) were added to 600-ml quantities of solution containing

TABLE 7.—*Extractions of bauxites with solutions containing 125 g of sodium hydroxide per liter and various amounts of sodium salts* [a]

Experiment	Bauxite		Salt added		Temperature	Al_2O_3 in solution	SiO_2 in solution	Extraction of Al_2O_3 [b]	$\frac{SiO_2}{Al_2O_3} \times 100$ in solution
	Designation	Amount used	Kind	Amount					
		g/liter		g/liter		g/liter	g/liter	%	
1	B	180		None	Boiling	50.2	0.228	63.2	0.45
2	B	180	Na_2SO_4	125	do	50.2	.105	63.2	.21
3	B	180	Na_2SO_4	250	do	50.0	.090	63.0	.18
4	B	180	Na_2SO_4	375	do	48.2	.080	60.6	.17
5	B	180		None	150° C	48.8	.172	61.5	.35
6	B	180	Na_2SO_4	250	150° C	50.2	.046	63.2	.09
7	B	180	NaBr	125	Boiling	49.4	.140	62.2	.28
8	B	180	NaBr	250	do	45.6	.078	57.4	.17
9	B	180	NaBr	375	do	48.3	.061	60.8	.13
10	B	180	NaBr	500	do	49.8	.025	62.7	.05
11	B	180	NaBr	250	150° C	50.2	.046	63.2	.09
12	B	180	NaCl	125	Boiling	46.4	.085	58.4	.19
13	B	180	NaCl	250	do	47.2	.048	59.3	.10
14	B	180	NaCl	375	do	47.5	.031	59.7	.07
15	B	180	NaCl	500	do	46.3	.028	58.2	.06
16	B	180	NaCl	125	150° C	43.9	.054	55.3	.12
17	B	180	NaCl	250	150° C	37.5	.017	43.5	.05
18	B	130	NaCl	375	150° C	50.1	.016	63.1	.03
19	B	180	$NaNO_3$	125	Boiling	49.1	.048	62.0	.10
20	B	180	$NaNO_3$	250	do	48.7	.010	61.5	.02
21	B	180	$NaNO_3$	375	do	48.4	.013	61.1	.03
22	B	180	$NaNO_3$	125	150° C	46.2	.036	58.2	.08
23	B	180	$NaNO_3$	250	150° C	49.4	.009	62.2	.02
24	B	180	$NaNO_3$	375	150° C	42.6	.008	53.7	.02
25	C	157.5		None	Boiling	54.0	.324	67.9	.60
26	C	157.5	Na_2SO_4	125	do	54.0	.135	67.8	.25
27	C	157.5	Na_2SO_4	250	do	52.7	.102	66.2	.19
28	C	157.5	Na_2SO_4	375	do	49.4	.080	62.0	.16
29	C	157.5	Na_2SO_4	500	do	53.8	.071	67.8	.13
30	C	157.5	Na_2SO_4	250	150° C	53.0	.053	66.7	.10
31	C	157.5	NaBr	250	Boiling	47.7	.076	60.0	.16
32	C	157.5	NaCl	125	do	51.3	.169	64.5	.33
33	C	157.5	NaCl	250	do	51.2	.113	64.4	.22
34	C	157.5	NaCl	375	do	50.4	.071	63.4	.14
35	C	157.5	NaCl	500	do	50.5	.056	63.4	.11
36	C	157.5	NaCl	250	150° C	48.2	.021	60.6	.04
37	C	157.5	$NaNO_3$	250	Boiling	47.1	.057	59.3	.12
38	C	157.5	$NaNO_3$	250	150° C	51.8	.018	65.2	.03
39	D	142		None	Boiling	61.8	.340	77.4	.55
40	D	142	NaCl	125	do	59.2	.102	74.4	.17
41	D	142	NaCl	250	do	56.8	.069	71.5	.12
42	D	142	NaCl	375	do	52.6	.032	66.2	.06
43	D	142		None	150° C	61.3	.215	77.0	.35
44	D	142	NaCl	250	150° C	56.0	.024	70.2	.04

[a] Extracted by heating for 3 hr. [b] Based on original volume of extracting solution (400 ml).

75 g of NaOH and 150 g of NaCl, NaBr, $NaNO_3$, or Na_2SO_4. The mixtures were kept in the autoclave at 150° C for 5 days and were shaken twice daily. The resulting products were then filtered, washed thoroughly with hot water, alcohol, and ether, and dried at 110° C overnight. Analysis of the preparations gave the results shown in table 8.

The compositions of the chloride, bromide, and nitrate double salts in table 8 are similar to that of sodalite and the composition of the sulfate compound corresponds approximately with noselite. All the synthetic preparations contain less sodium salt than corresponds to the theoretical compositions and are hydrated, whereas the pure compounds should be anhydrous.

TABLE 8.—*Composition of sodalite-type compounds* [a]

Experiment	Sodium salt (NaX^b) in molecule	Oxide composition					Molar ratios				
		Na_2O	Al_2O_3	SiO_2	X[c]	H_2O	Na_2O	Al_2O_3	SiO_2	NaX^b	H_2O
		%	%	%	%	%					
1	None	21.97	30.74	35.54	------	11.46	1.17	1.00	1.96	------	2.1
2	NaCl	22.71	30.28	35.20	5.53	5.76	0.96	1.00	1.97	0.53	1.1
3	NaBr	22.39	29.80	33.46	11.45	3.43	.99	1.00	1.91	.49	0.7
4	$NaNO_3$	21.22	32.06	34.64	8.24	3.64	.85	1.00	1.83	.49	.6
5	Na_2SO_4	22.14	29.86	34.18	6.53	7.12	.94	1.00	1.94	.28	1.3

[a] Prepared from mixtures (heated at 150° C for 5 days) of 26 g of gibbsite and 20 g of SiO_2 as silica gel ($1Al_2O_3:2SiO_2$, molar) in 600 ml of solution containing 75 g of NaOH and 150 g of NaCl, NaBr, $NaNO_3$, or Na_2SO_4.
[b] NaX = NaCl, NaBr, $NaNO_3$, or Na_2SO_4.
[c] X = Cl, Br, NO_3, or SO_4.

Table 9 shows the results of comparisons of the X-ray diffraction patterns of the various synthetic preparations and of the extraction residues from bauxite C with the pattern of natural sodalite. The patterns of the separate compounds within groups 1, 2, 3, 4, and 5 were identical with each member of the group, but each group pattern differed in various degrees from the pattern of sodalite. In the case of the NaBr preparations, the patterns were different from that of sodalite only in indicating a slightly larger unit-cube size, whereas for the $NaNO_3$ preparations, slight variations from the sodalite pattern were noted. The sulfate preparation had a pattern different from that of sodalite and also from that of naturally occurring noselite. Unexpectedly, the pattern of the residue of bauxite C, extracted with NaOH-Na_2SO_4 solution, fell in group 5 with sodium aluminum silicate hydrate and showed no similarity to the pattern of the synthetic sulfate compound.

TABLE 9.—*Comparison of X-ray diffraction patterns of sodalite-type compounds*

Experiment	Sodium salt in molecule	Source of preparation	Degree of similarity with X-ray pattern of sodalite as given in literature
1a	NaCl	Natural sodalite, Canada	Identical.
1b	do	Synthetic	Do.
1c	do	NaOH-NaCl extraction residue of bauxite C	Do.
2a	NaBr	Synthetic	Almost identical.
2b	do	NaOH-NaBr extraction residue of bauxite C	Do.
3a	$NaNO_3$	Synthetic	Very similar.
3b	do	NaOH-$NaNO_3$ extraction residue of bauxite C	Do.
4	Na_2SO_4	Synthetic	Different.
5a	None	do	Do.
5b	do	NaOH extraction residue of bauxite C	Do.
5c	Na_2SO_4	NaOH-Na_2SO_4 extraction residue of bauxite C	Do.

4. COMPARISON OF EFFECTIVENESS OF VARIOUS SALTS IN DEPRESSING THE CONCENTRATION OF SILICA IN SODIUM ALUMINATE SOLUTIONS

These experiments suggested that the decreased concentrations of silica obtained in sodium aluminate solutions in the presence of sodium carbonate might be caused by the formation of a compound similar to sodalite and having a lower solubility than that of the sodium aluminum silicate formed in the absence of sodium carbonate. They

suggested also that under the conditions of extraction other sodium salts, particularly sodium chloride, might form sodalitic-type compounds, possibly having lower solubilities than the carbonate compound. Accordingly, the investigation was extended to determine which sodium salt would be more effective in depressing the solubility of silica in sodium aluminate solutions.

A considerable number of extractions of bauxites B, C, and D were made with a solution containing 125 g of NaOH per liter and various added salts in the amounts shown in table 7. Exactly the same procedure was followed in these experiments as in those reported in table 5.

Figures 2 to 7, based on data in tables 5 and 7, indicate the purity of the Al_2O_3 in solution with respect to SiO_2 in the presence of the various salts. It is evident that sodium nitrate is the most effective, of the salts tried, in reducing the concentration of SiO_2 in the sodium aluminate extracts. Next in order are the halide salts, and of these the chloride is shown to be more effective than the bromide where comparable data are available. The behavior of sodium sulfate and sodium carbonate is somewhat erratic, but in most cases the former causes the larger reductions in the concentration of SiO_2. Generally, the amounts of SiO_2 found in the 150° C extracts are considerably lower than those obtained at boiling at atmospheric pressure, but with bauxite B in the presence of $NaNO_3$, boiling appears to be almost as effective as treatment at 150° C.

The economic advantages and effectiveness of sodium chloride are such that it seemed desirable, in the remainder of this investigation, to concentrate on the use of common salt as a desilication agent.

5. PILOT-PLANT EXTRACTIONS

A number of extractions of bauxites B, C, and D were made in a small pilot plant. This equipment consisted of 30-gallon iron digester fitted with a mechanical stirrer and having steam, water, and air inlets. The digester was connected with a filter press from which the filtrate flowed to two 50-gallon storage drums. A centrifugal pump in the circuit permitted transfer of the solution from one storage drum to another or back to the digester.

The quantities of materials used and data obtained in some representative extractions are given in table 10. The solution containing sodium hydroxide and dissolved sodium salt was heated to boiling by passing steam into the digester. The bauxite then was added, and the mixture was heated at the desired temperature for 3 hours while stirring constantly. In experiments 1, 2, and 3 of table 10 the extractions were made at atmospheric pressure and, in experiments 4, 5, and 6, at approximately 30-lb/in.^{2} gage pressure (135° C). At the completion of the heating period each mixture was filtered, the filter cake thoroughly washed with hot water, and the volume of the extract plus wash water determined. Analyses of the solutions were made for Na_2CO_3, NaOH, Al_2O_3, and SiO_2.

It will be noted that the recoveries of Al_2O_3 reported in table 10 are slightly lower than those obtained in laboratory-scale extractions. This was caused by an accumulation of minor losses that could not be avoided in the pilot plant setup. The percentages of silica in experiments 4, 5, and 6, based on the Al_2O_3 content of the solutions,

TABLE 10.—*Pilot-plant extractions of bauxites* [a]

Experiment	Bauxite		Salt added		NaOH added	Volume of—		Composition of extract plus wash				Recoveries of—			$\frac{SiO_2}{Al_2O_3}\times 100$ in solution	$\frac{SiO_2}{Al_2O_3}\times 100$ in precipitated $Al_2O_3 \cdot 3H_2O$
	Designation	Quantity used	Kind	Amount		Initial solution	Extract plus wash	$NaCO_3$	NaOH	Al_2O_3	SiO_2	$NaCO_3$	NaOH	Al_2O_3		
		lb		*lb*	*lb*	*gal*	*gal*	*g/liter*	*g/liter*	*g/liter*	*g/liter*	%	%	%		
1	B	20.0	$NaCO_3$	27.8	13.9	13.1	22.9	77.5	39.2	18.6	0.046	75	77	58	0.25	0.20
2	D	17.25	do	30.0	15.0	13.2	29.4	105.4	56.0	29.8	.089	86	92	75	.30	.27
3	D	17.25	do	30.0	15.0	14.0	36.4	81.3	43.8	22.6	.072	82	89	71	.32	.21
4	C	15.8	NaCl	25.0	12.5	11.0	25.5	----	----	24.5	.034	----	----	60	.14	.14
5	C	13.8	do	37.5	12.5	10.9	21.4	----	----	26.7	.024	----	----	60	.09	.09
6	C	12.6	$NaNO_3$	20.0	10.0	9.0	30.3	----	----	14.2	.013	----	----	63	.09	.09

[a] Experiments 1, 2, and 3 were made at the boiling temperatures of the solutions at atmospheric pressure, and experiments 4, 5, and 6 at 135° C (30-lb gage pressure). Time of extraction was 2 hr.

are plotted in figure 3. These values are comparable with those obtained in the small-scale extractions.

On completion of each extraction, the combined filtrate and wash contained in the storage drum was heated to boiling. Carbon dioxide was then passed slowly into the solution, which was kept in continuous agitation. Addition of carbon dioxide was continued over a period of 8 to 10 hours, until less than 0.5 g of Al_2O_3 per liter remained in solution. The mixture of precipitate and solution was then pumped into the digester, from which it was filtered on the filter press, and the precipitate was washed four times with 10-gallon portions of hot water. The material was removed from the filter press and dried overnight.

Microscopical examinations of the products showed that they consisted of irregular or prismatic crystals having the refractive indices of gibbsite. Analyses of the material for SiO_2 and Al_2O_3 gave the ratios shown in the last column of table 10. These values are the same or somewhat lower than those for the solutions before precipitation of the alumina. The soda contents of gibbsite from experiments 2 and 3 were 0.3 and 0.4 percent, respectively, and the Fe_2O_3 content of the latter was 0.09 percent. This relatively high value for Fe_2O_3 was undoubtedly caused by mechanical contamination. This was extremely difficult to prevent because the same equipment had to be used both for the extractions and for precipitation and handling of the hydrated alumina.

The precipitation of alumina from silica by differential precipitation was not investigated as this problem has received considerable study in connection with commercial operation of the Bayer process. McCulloch [7] has shown that by means of carbon dioxide, alumina containing 0.02 to 0.03 percent of silica can be precipitated from solutions containing 75 to 80 g of Al_2O_3 and 0.15 to 0.25 g of SiO_2 per liter, provided precipitation is stopped when about 75 percent of the alumina has been removed from solution.

As separation of alumina from silica by differential precipitation is most effective when the alumina concentration is high, extracts similar to those obtained in this study should not be diluted by excessive quantities of wash water prior to separation of the alumina.

6. RECOVERY OF SODA AND ALUMINA FROM BAUXITE-EXTRACTION RESIDUES

A number of experiments were performed on the recovery of Na_2O and Al_2O_3 from the bauxite-extraction residues. As shown previously, such residues contain Na_2O, Al_2O_3, and SiO_2 in molar ratios approximating 1:1:2 as an insoluble sodium aluminum silicate complex.

In most of the experiments, the residues were mixed with approximately the quantities of $CaCO_3$ required to form dicalcium silicate with the silica, leaving the Na_2O and Al_2O_3 as sodium aluminate. A few mixtures were also prepared in which lime and silica were present in molar ratios of 1 and 3. In some experiments, data for which are included in table 11, Na_2CO_3, as well as $CaCO_3$, was added. This was also done in the treatment of a bauxitic clay, experiment 11, table 11. The mixtures in 25 to 30-g quantities were heated in an electric furnace and held for 1 hour at the temperatures indicated in the table. The products were ground to pass a No. 80 sieve.

TABLE 11.—*Extractions of Al_2O_3 and Na_2O from sinters prepared from bauxite-extraction residues*

Experiment	Material	Temperature of heating[a]	Composition of sinter					Molar ratio CaO/SiO_2 in sinter	Molar ratio Na_2O/Al_2O_3 in sinter	Extraction[b] of—		$\frac{SiO_2}{Al_2O_3} \times 100$ in solution
			CaO	SiO_2	Al_2O_3	$Fe_2O_3+TiO_2$	Na_2O			Na_2O	Al_2O_3	
		°C	%	%	%	%	%			%	%	
1	Residue from B	1,260	24.2	25.9	26.1	4.7	17.0	1.0	1.0	2	0	
2	do	1,200	33.7	20.9	22.7	3.9	13.1	2.0	1.0	85	62	2.05
3	do	1,300	40.4	21.5	19.3	4.8	12.0	2.0	1.0	92	81	1.23
4	do	1,325	50.4	17.8	16.0	3.9	10.4	3.0	1.1	62	2	
5	Residue from C	1,260	22.5	24.2	32.8	5.9	14.5	1.0	0.7	3	0	
6	do	1,225	30.8	19.7	26.8	4.8	12.2	2.0	.8	97	68	
7	do	1,225	35.2	18.9	25.6	4.6	[c] 15.3	2.0	1.0	93	82	
8	do	1,230	32.6	17.5	23.8	4.3	[c] 20.5	2.0	1.4	67	87	
9	Residue from D	1,300	38.9	20.8	19.6	11.4	8.9	2.0	0.8	94	55	1.42
10	do	1,325	48.9	17.4	16.4	9.5	7.0	3.0	.7	47	0	
11	Bauxitic clay	1,225	25.8	13.8	33.5	3.8	[c] 22.0	2.0	1.1	88	85	0.23

[a] Heated for 1 hr. and ground to pass No. 80 sieve.
[b] Two-gram samples of the sinters were extracted by boiling for 2 hrs with 100-ml quantities of water.
[c] Na_2CO_3 added to raw mix before calcination.

Two-gram samples of the sinters were extracted by boiling for 2 hours with 100-ml quantities of water. The results in table 11 show that the CaO/SiO_2 ratio is rather critical and that at values of 1.0 and 3.0 the amounts of Al_2O_3 and Na_2O extracted are sharply reduced from the quantities obtained at a CaO/SiO_2 molar ratio of 2.0. When Na_2O and Al_2O_3 are present in molar ratios below unity, unsatisfactory extractions of Al_2O_3 are obtained even at the optimum molar ratios of CaO to SiO_2 (experiments 6 and 9).

A quantity of sinter No. 3, table 11, was calcined at 1,300° C for 1 hour, and the product ground to pass a No. 80 sieve. Samples of the sinter were extracted with 100-ml portions of solutions containing the amounts of NaOH shown in table 12. At temperatures below boiling, mechanical stirring was employed.

The percentage extractions of Al_2O_3 and Na_2O from this sinter are only slightly affected by an increase in the amount of sinter treated from 50 to 200 g/liter. For an agitation period of 30 minutes, the maximum extractions of Na_2O and Al_2O_3 are about 90 and 85 percent, respectively.

TABLE 12.—*Extraction of* Al_2O_3 *and* Na_2O *from sinter prepared from residue of bauxite B and ground to pass a No. 80 sieve*

[Volume of extracting solution, 100 ml; mechanical stirring used at temperatures below boiling.]

Experiment	NaOH in extracting solution	Weight of sample extracted	Temperature of extraction	Time of extraction	Extraction of—		$\frac{SiO_2}{Al_2O_3}\times 100$ in solution
					Na_2O	Al_2O_3	
	g/liter	*g/liter*	*° C*	*min*	%	%	
1	0	50	50	30		65	
2	2	50	50	30		76	
3	10	50	50	30		83	
4	0	50	85	30	91	72	
5	0	200	85	30	90	72	0.33
6	2	50	85	30		85	
7	12	50	85	30		85	
8	100	50	85	30		82	
9	12	200	85	30		80	.73
10	0	50	Boiling	1	81	69	
11	2	50	do	1		66	
12	0	50	do	120	91	71	
13	2	50	do	120		79	
14 *	0	50	70	30		84	1.93
15 *	0	200	70	30		82	2.42

* In these experiments the extracting solution contained 150 g of Na_2CO_3 and 200 g of NaCl per liter. Sinter ground to pass a No. 200 sieve.

Experiments 14 and 15, table 12, were made to determine the effect of high concentrations of Na_2CO_3 and NaCl in the extracting solution on the recovery of Al_2O_3 from the sinter. The samples of sinter used in these experiments were ground to pass a No. 200 sieve. It is evident that the high concentrations of the salts do not diminish the recovery of Al_2O_3 from the sinter. This fact makes it possible to use the spent solution from the initial extraction of the bauxite for extraction of the soda-lime sinter prepared from the bauxite-extraction residue, as will be illustrated in the following section.

The data contained in this section obviously do not represent a thorough study of the soda-lime-sinter method of alumina extraction. This process has recently received considerable study elsewhere [8].

7. FLOW SHEET AND SUMMARY OF PROCESS

A suggested commercial process for the extraction of alumina from high-silica bauxites, developed from experiments described in the preceding sections, is illustrated by a flow sheet, figure 8.

The composition of the bauxite shown in the flow sheet is approximately that of bauxite C, with minor constituents such as Fe_2O_3 and TiO_2, omitted for simplification. The finely ground material is digested for a suitable time with a sodium hydroxide-sodium chloride solution, either at the boiling temperature of the solution at atmospheric pressure or at a higher temperature and pressure. On completion of the heating period, the mixture is filtered and the residue washed with water or salt solution. Washing need not be thorough because the residue is reserved for further treatment to recover the soda and alumina that it contains.

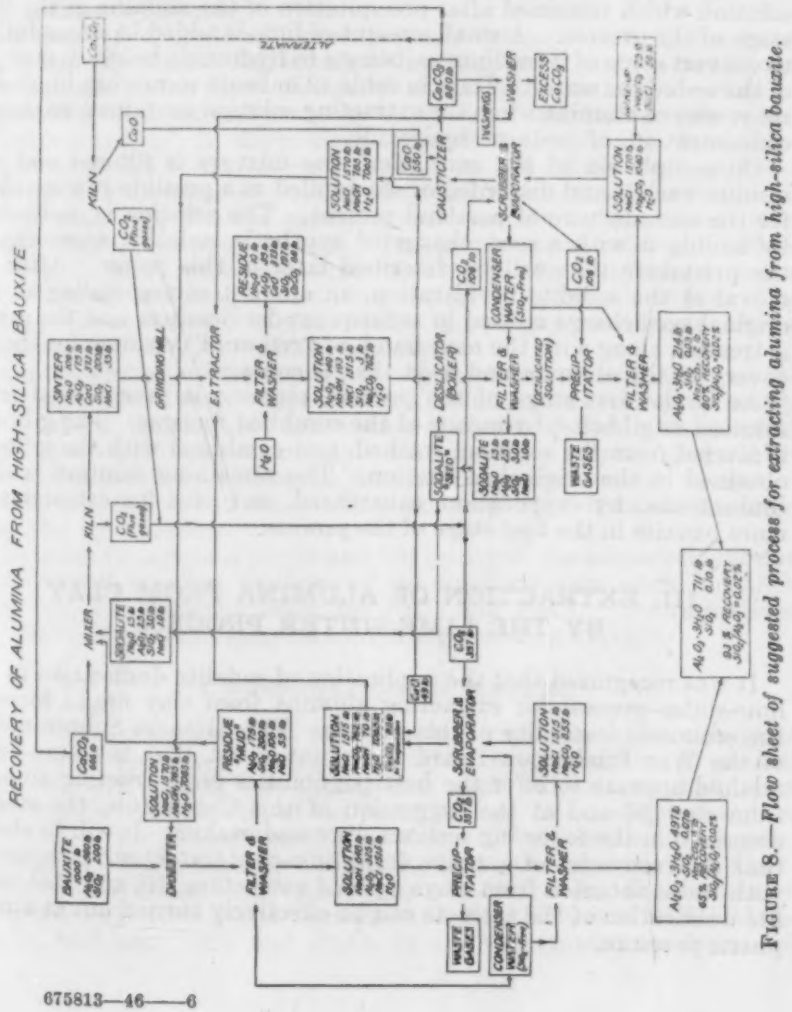


FIGURE 8.—*Flow sheet of suggested process for extracting alumina from high-silica bauxite.*

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The alumina may be removed from the extract by controlled precipitation with carbon dioxide in the presence of a seed charge of gibbsite. In the flow sheet the scrubbed gas is shown as the source of carbon dioxide. By passing the kiln gas into the solution, the major part of the alumina can be precipitated without undue contamination by the small amount of silica in the extract. In the flow sheet, complete precipitation of the alumina is indicated as this would be accomplished in cyclical operation of the process.

The residue from the initial extraction contains soda, alumina, silica, and sodium chloride in proportions approaching those of the mineral sodalite, as well as the relatively inert constituents of the bauxite, such as Fe_2O_3 and TiO_2. Ground limestone is added to the residue to give a CaO/SiO_2 molar ratio of 2.0, and the mixture is then heated to a suitable temperature to bring about clinkering or sintering. After grinding the sinter, it is extracted at 70° to 80° C with the solution which remained after precipitation of the alumina in the first stage of the process. A small amount of lime is added to this solution to convert some of its sodium carbonate to hydroxide before extraction of the soda-lime sinter. Data in table 12 indicate somewhat improved recoveries of alumina when the extracting solution contains a moderate concentration of sodium hydroxide.

On completion of the extraction, the mixture is filtered and the residue washed and discarded or stock-piled as a possible raw material for the manufacture of portland cement. The solution is desilicated by boiling it with a seed charge of synthetic sodalite, according to the procedure that will be described later in this paper. After removal of the sodalite by filtration, an amount corresponding to the original seed charge is used in subsequent desilications and the excess is treated, along with the next batch of "red-mud" residue, for the recovery of the alumina and soda that it contains.

As in the first stage of the process, alumina is precipitated from solution as gibbsite, by means of the scrubbed flue gas. The gibbsite is filtered from the solution, washed, and combined with the gibbsite obtained in the original extraction. The remaining solution is then concentrated by evaporation, causticized, and used for extraction of more bauxite in the first stage of the process.

III. EXTRACTION OF ALUMINA FROM CLAY BY THE LIME-SINTER PROCESS

It was recognized that the application of sodalite desilication to the lime-sinter process for extracting alumina from clay might increase the economic feasibility of this process. The Alumina Subcommittee of the War Production Board has pointed out that the lime-sinter method appears to offer the best possibilities for extracting alumina from clay [9] and at the suggestion of this Committee, the studies described in the following sections were undertaken. It will be shown that the recoveries of alumina from lime-clay sinters are comparable with those obtained from clays by acid extraction [10] and that sodalite desilication of the extracts can be effectively carried out at atmospheric pressure.

1. MATERIALS AND PROCEDURE

The raw materials were a Georgia kaolin and a ground limestone of the following compositions:

	Kaolin, %	Limestone, %
SiO_2	45.77	0.88
Al_2O_3	37.23	.12
Fe_2O_3	1.00	.21
TiO_2	1.12	-----
CaO	-----	54.98
MgO	-----	0.35
Na_2O	0.06	-----
Loss on ignition	14.01	43.44
Total	99.19	99.98

The other materials included sodium carbonate, sodium chloride, and sodium hydroxide.

Sinters were prepared from properly proportioned mixtures of the ground limestone and kaolin by burning under various conditions. Extractions of the finely powdered sinters were made with solutions containing sodium carbonate or mixtures of sodium carbonate and sodium chloride. In the preliminary experiments listed in the following section the mixtures were agitated in 750-ml Erlenmeyer flasks placed on a slow-speed shaking machine which was kept in an air thermostat. In all other experiments, extractions of the sinters were made with a high-speed stirrer. The extraction vessel was a 500-ml three-neck flask, with the stirrer inserted in the middle neck and a thermometer and funnel for adding the sinter in the side necks. The temperature was maintained within ± 1 degree centigrade of the values specified, by controlled heating.

On completion of the extraction, the mixtures were filtered and the residues washed with water or NaCl solution. In the preliminary experiments the extracts and washes were mixed, but in subsequent work they were stored separately. The combined extracts and washes were desilicated by boiling in iron containers with seed charges of synthetic sodalite, and the solutions were separated from the insoluble material by filtration.

In order to ascertain yields and the purity of the extracted alumina with respect to silica, analyses of the solutions were made for Al_2O_3 and SiO_2 and, in some cases, for Na_2O and NaCl. Determinations of SiO_2 were made in samples containing 5 to 10 g of Al_2O_3.

2. PREPARATION OF SINTERS

To obtain a sinter which would be free from unreactive aluminate compounds such as gehlenite, $2CaO.Al_2O_3.SiO_2$, a mixture of ground limestone and kaolin was prepared in such proportions that, after burning, the composition of the resulting material corresponded to a point on a line joining the composition of $2CaO.SiO_2$ and the quintuple point $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, and $2CaO.SiO_2$ in the CaO-Al_2O_3-SiO_2 diagram [16]. Allowance was made for the lime and alumina required for the formation of $CaO.TiO_2$ and $4CaO.Al_2O_3$-Fe_2O_3 with any TiO_2 and Fe_2O_3 in the raw materials. About 80

pounds of this mixture were burned in a brick kiln at 1,300° to 1,350° C for 5 hours. The composition of this product, which will be referred to as sinter R, was

	%
SiO_2	22.82
Al_2O_3	18.38
Fe_2O_3	0.70
TiO_2	.64
CaO	56.84
MgO	0.56
Na_2O	.10
Loss on ignition	.11
Total	100.15

Because preliminary experiments showed that this product did not give satisfactory extractions, it was ground to an average particle size of 5 microns.

A number of small-batch sinters were prepared by burning 100-g quantities of the original mix in a muffle until the products gave no test for free lime. This material (sinter S) was only slightly sintered and required no grinding. It contained dicalcium silicate largely in the beta form.

A third batch of lime-clay calcine (sinter T) was obtained. Details of the preparation of this material were not available. Petrographic examination of the sinter showed the presence of about three times as much gamma- as beta-dicalcium silicate. The beta-dicalcium silicate grains appeared to be surrounded by thin films of low-index, isotropic material, presumably glass. The composition of the sinter was

	%
SiO_2	22.38
Al_2O_3	18.00
Fe_2O_3	1.34
TiO_2	0.98
CaO	54.44
MgO	0.99
Na_2O	.76
Loss ignition	1.15
Total	100.04

3. EXTRACTION OF SINTERS WITH DILUTE SODIUM CARBONATE SOLUTIONS

The extractions listed in table 13 were made on samples of sinter S. The volume of the extracting solution was 400 ml in all experiments and the quantity of material extracted was such that the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was 2.0. The mixtures were shaken for 2 hours at the temperatures indicated in table 13, filtered, and the residues washed with 100 ml of hot water. Some of the combined extracts and washes were then analyzed for Al_2O_3 and SiO_2, giving the results shown in table 13 under the heading "Not desilicated." Other combined extracts and washes were boiled for 2 hours with seed charges consisting of 5 g of synthetic sodalite. After removal of the sodalite by filtration, the solutions were analyzed for Al_2O_3, SiO_2, and in some cases, Na_2O. The results of determinations of Al_2O_3 and SiO_2 and calculated recoveries of Na_2O are given in the last five columns of table 13.

TABLE 13.—*Extractions of sinter S with dilute* Na_2CO_3 *solutions containing* NaCl

[Volume of extracting solution, 400 ml; time of extraction, 2 hr]

Experiment	Composition of extracting solution		Quantity of sinter used	Temperature of extraction	Composition of extracts plus washes, and percentage of Al_2O_3 recovered							Recovery of Na_2O in desilicated solution
					Not desilicated				Desilicated			
	Na_2CO_3	NaCl			Al_2O_3 concentration	Al_2O_3 recovered	SiO_2	$\frac{SiO_2}{Al_2O_3}\times 100$	Al_2O_3 concentration	Al_2O_3 recovered	SiO_2	$\frac{SiO_2}{Al_2O_3}\times 100$	
	g/liter	*g/liter*	*g/liter*		*g/liter*	%	*g/liter*		*g/liter*	%	*g/liter*		%
1	100	0	261	35° C	31.7	80	0.761	2.4					
2	100	160	261	35° C	28.6	72	1.067	3.8					
3	50	0	130	50° C	15.8	81	0.411	2.6					
4	50	40	130	50° C					14.6	76	0.035	0.24	
5	50	80	130	50° C	15.0	78	.285	1.9	14.6	76	.023	.16	98
									14.8	77	.016	.10	99
6	50	120	130	50° C					14.2	74	.014	.10	97
7	50	160	130	50° C					13.3	69	.007	.05	
8	100	0	261	50° C	31.8	80	.763	2.4	30.4	79	.082	.27	98
9	100	160	261	50° C	27.3	71	.546	2.0	26.9	70	.027	.10	97
10	100	240	261	50° C					25.0	65	.022	.09	
11	100	160	261	85° C					10.3	26	.016	.16	
12	50	0	130	Boiling	13.5	70	.216	1.6					
13	100	160	130	do					9.5	24	.017	.18	

It will be noted that the initial extracts contained SiO_2 in amounts corresponding to 1.6 to 3.8 percent of the weight of Al_2O_3 in solution. For extractions made at 50° C the purity of Al_2O_3 with respect to SiO_2 in the desilicated solutions increased as the ratio of NaCl to Na_2CO_3 increased, but the higher concentrations of NaCl caused diminished recoveries of Al_2O_3 in the initial extractions. The higher extractions of Al_2O_3 were obtained at both 35° and 50° C.

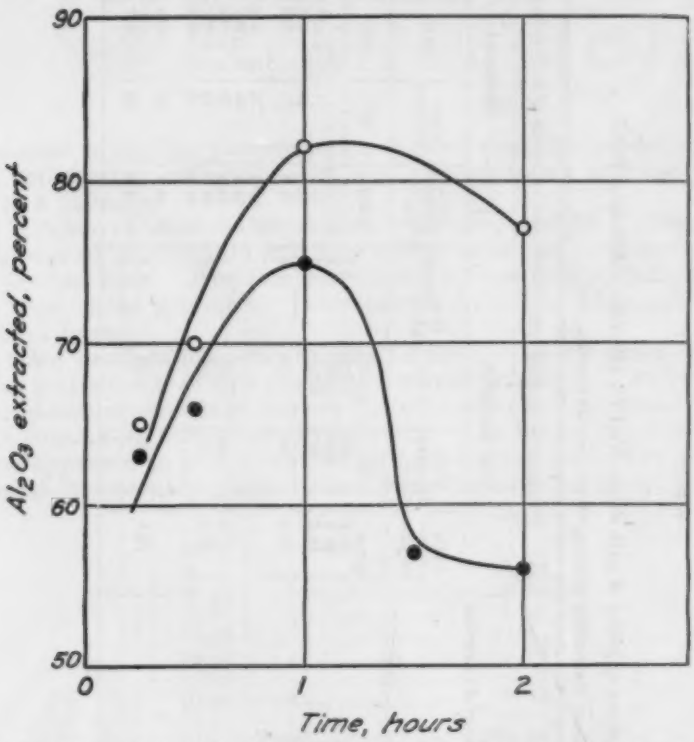

FIGURE 9.—*Effect of time of extraction at 40° C on the recovery of alumina from sinter R.*

The extracting solutions contained 50 g/liter of Na_2CO_3, 200 g/liter of NaCl (open circles); and 100 g/liter of Na_2CO_3, 200 g/liter of NaCl (closed circles). Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter = 2.5

Although the data of table 13 indicate that the losses of soda amounted to 2 to 3 percent, it should be mentioned that these values are not particularly accurate, because of the very small aliquots of solution that had to be taken. A better method of measuring soda losses is by analysis of the solid residues. Such analysis indicated a loss of 0.05 percent of NaCl and 1.5 percent of Na_2CO_3. With some raw materials this loss in sodium carbonate might be made up, wholly or in part, by the amount of alkali usually found in clay.

The results of experiments on sinter R, which were made to determine the optimum values for time of extraction and molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter, are shown in figures 9 and 10, respectively. Both 5- and 10-percent Na_2CO_3 solutions, containing 200 g of NaCl per liter, were used and the extraction temperature

was 40° C. In the experiments illustrated by figure 9 the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was maintained constant at 2.5.

As shown in figure 9 the optimum extraction time appears to be about 1 hour. Longer periods gave much reduced extractions for the 10-percent Na_2CO_3 solution, appreciable reductions for the 5-percent solution. It should be pointed out, however, that the optimum

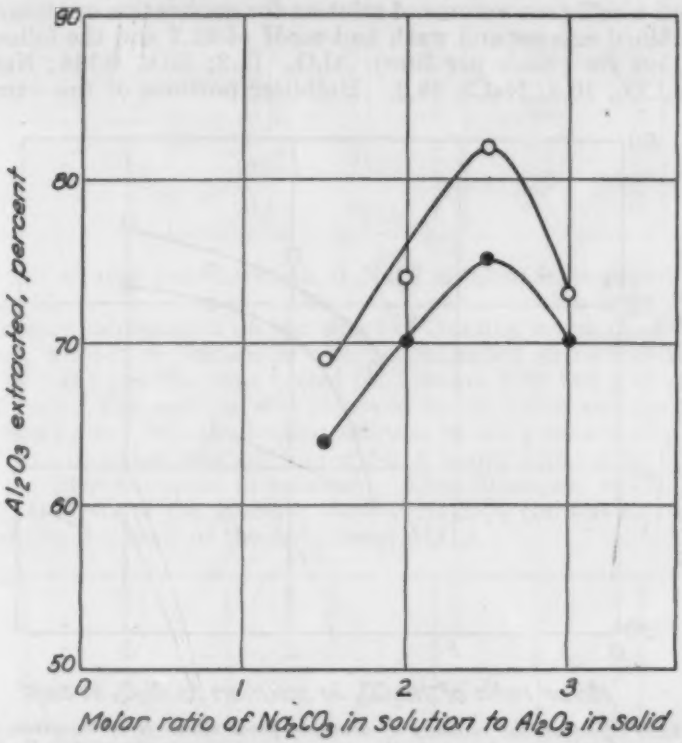

FIGURE 10.—*Effect on the recovery of alumina from sinter R of variation of the molar ratio of sodium carbonate in the extracting solution to alumina in the sinter.*

The extracting solutions contained 50 g/liter of Na_2CO_3, 200 g/liter of NaCl (open circles); and 100 g/liter of Na_2CO_3, 200 g/liter of NaCl (closed circles). Mixtures shaken for 1 hr at 40° C.

time of extraction will be determined by the type of agitator used as well as by the nature of the sinter. In a later section it will be shown that when more vigorous agitation was employed the optimum extraction period was considerably less than that indicated in figure 9.

Figure 10 shows that a molar ratio of $2.5Na_2CO_3/Al_2O_3$ gave the highest extractions of alumina from sinter R, with a marked decrease occurring at a $3.0Na_2CO_3/Al_2O_3$ molar ratio.

The effect of excess sodium hydroxide on extractions of alumina from sinter R is shown by comparison of figures 10 and 11. The compositions of the mixtures in the experiments illustrated by figure 11 were the same as those on which figure 10 is based, except that they contained a quantity of added NaOH, which corresponded to

10 percent of the weight of Na_2CO_3 in the initial solutions. Poorer extractions were obtained in these experiments than in comparable ones shown in figure 10, except where the molar ratio of Na_2CO_3 to Al_2O_3 was 3.0.

4. DESILICATION OF DILUTE SODIUM ALUMINATE SOLUTIONS

An extraction of sinter R was made in the small pilot plant in order to prepare a sufficient volume of solution for desilication experiments. The combined extract and wash had a pH of 12.7 and the following composition (in grams per liter): Al_2O_3, 14.2; SiO_2, 0.144; NaOH, 18.6; Na_2CO_3, 10.9; NaCl, 68.2. Half-liter portions of this extract,

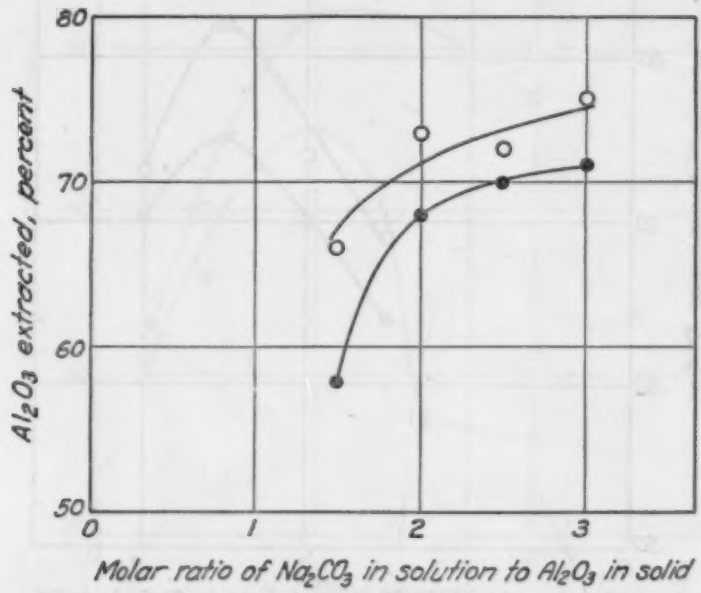

FIGURE 11.—*Effect on the recovery of alumina from sinter R of variation of the molar ratio of sodium carbonate in the extracting solution to alumina in the sinter, in the presence of sodium hydroxide.*

The extracting solutions contained 50 g/liter of Na_2CO_3, 5 g/liter of NaOH, 200 g/liter of NaCl (open circles); and 100 g/liter of Na_2CO_3, 10 g/liter of NaOH, 200 g/liter of NaCl (closed circles). Mixtures shaken for 1 hr at 40° C.

with and without added sodium chloride, were boiled with seed charges of synthetic sodalite prepared in the autoclave from gibbsite plus silica gel. The seed was removed by filtration, and the solutions were analyzed. The results are summarized in table 14.

When the quantity of seed added was 2 g/liter, the greatest lowering in SiO_2 concentration was obtained after boiling for 2 to 3 hours, as shown in experiments 2 to 5. This quantity of seed is insufficient, however, and if the amount of sodalite is increased to 10 g/liter, the desilication proceeds further, as shown in experiment 6. Increases in the concentration of NaCl in solution also bring about decreases in the SiO_2 concentration (experiments 7 to 10). The values of the SiO_2/Al_2O_3 ratio, both in the solution and in the alumina after complete precipitation by means of carbon dioxide, are shown in figure 12.

TABLE 14.—*Desilication (by boiling with synthetic sodalite) of dilute sodium aluminate solution containing 14.2 g of Al_2O_3, 0.144 g of SiO_2 per liter, and various amounts of sodium chloride*

Experiment	NaCl in extracting solution	Amount of seed added	Time of boiling	SiO_2 in solution	$\frac{SiO_2}{Al_2O_3}\times 100$ in—	
					Solution	Precipitated Al_2O_3
	g/liter	g/liter	hr	g/liter		
1	68	0		0.1440	1.01	
2	68	2	0.5	.0442	0.31	
3	68	2	1	.0376	.26	
4	68	2	2	.0238	.17	
5	68	2	3	.0238	.17	
6	68	10	2	.0110	.08	0.10
7	114	10	2	.0100	.07	.07
8	162	10	2	.0049	.035	.05
9	204	10	2	.0047	.03	.04
10	243	10	2	.0024	.02	02

The point at zero concentration of NaCl is taken from experiment 3 of table 13.

To obtain information on the effect of treating larger quantities of solution, a 26-liter portion of the undesilicated extract containing 200 g of NaCl per liter was boiled for 2 hours with 260 g of sodalite (10 g/liter). The sodalite was removed by filtration and carbon dioxide was passed into the boiling solution in the presence of gibbsite seed. Precipitation was continued for 8 hours when only 0.1 g of Al_2O_3 per liter remained in solution. After filtration, washing, and drying, analysis of the gibbsite showed its SiO_2 content to be 0.014 percent (on the basis of the anhydrous Al_2O_3).

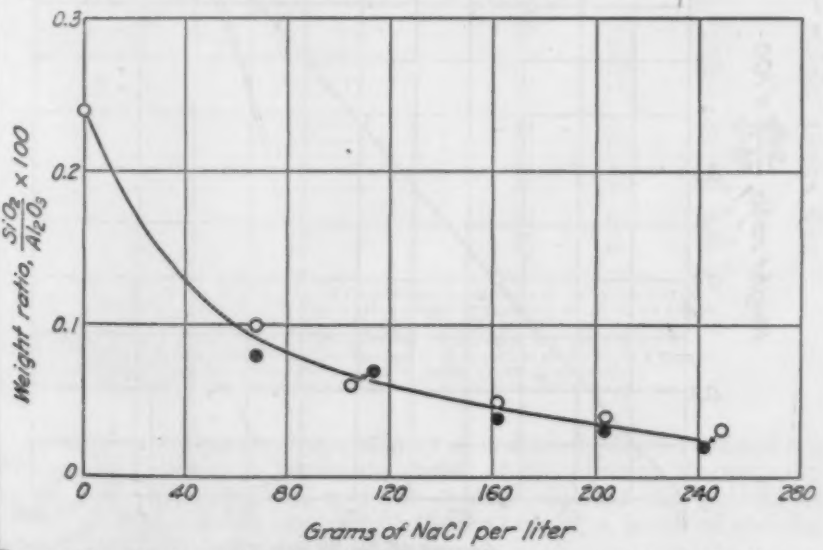

FIGURE 12.—*Effect of sodium chloride concentration on the sodalite desilication of an extract, from sinter R, containing 14 g/liter of Al_2O_3 and 0.14 g/liter of SiO_2.*

Values of $\frac{SiO_2}{Al_2O_3}\times 100$ determined by analysis of solutions (closed circles) and of hydrated alumina after complete precipitation from solution (open circles).

A few experiments were made in which various amounts of sodium hydroxide were added to portions of the extract described in the first paragraph of section C. After the pH of the resulting solutions had been measured, 500-ml portions were boiled for 2 hours with 5-g quantities of sodalite, the sodalite removed by filtration, and the

TABLE 15.—*Effect of sodium hydroxide concentration on the desilication of 500-ml portions of a sodium aluminate solution containing approximately 14 g of* Al_2O_3 *and 0.14 g of* SiO_2 *per liter*

[Desilication effected by boiling with 5 g of synthetic sodalite for 2 hr]

Experiment	NaOH in extracting solution	pH	Composition of solution after desilication		
			Al_2O_3	SiO_2	$\frac{SiO_2}{Al_2O_3} \times 100$
	g/liter		*g/liter*	*g/liter*	
1	18.6	12.7	14.2	0.011	0.08
2	69	13.4	14.0	.056	.4
3	119	14.0	14.5	.097	.67
4	169	14.2	14.8	.163	1.1
5	219	14.4	14.7	.174	1.2

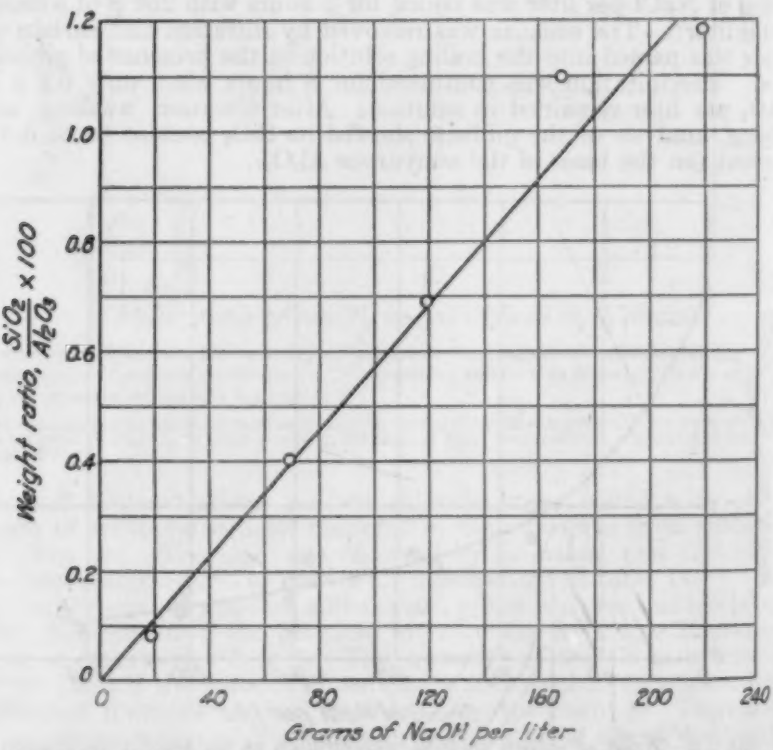

FIGURE 13.—*Effect of sodium hydroxide concentration on the sodalite desilication of an extract, from sinter R, containing approximately 14 g/liter of* Al_2O_3 *and 0.14 g/liter of* SiO_2.

solutions analyzed for Al_2O_3 and SiO_2. The data, given in table 15 and figure 13, show that desilication becomes less efficient as the sodium hydroxide concentration increases. Decomposition of the sodalite seed in the solutions containing the larger amounts of NaOH is indicated by increases in the Al_2O_3 contents of the solutions following desilication.

Thugutt [11] synthesized sodalite by autoclaving kaolinite at 212° C with a solution containing NaCl and NaOH. Other investigators have reported that sodalite is formed in fusions of large excesses of NaCl with (a) nephelite [12]; (b) mixtures of kaolinite and Na_2CO_3 [13]; or (c) mixtures of SiO_2, Al_2O_3, and NaOH [14].

As it had been observed in this study that some sodalite preparations were more effective desilicating agents than others, the various methods of preparation given in table 16 were tried.

TABLE 16.—*Comparison of desilication effectiveness of sodalites prepared by various methods*

[Initial solution contained 18.3 g of Al_2O_3 and 0.146 g of SiO_2 per liter. Desilication effected by boiling with sodalites for 1 hr]

Experiment	Method * of preparing sodalite	Quantity of sodalite used	NaCl added to solution	$\frac{SiO_2}{Al_2O_3}\times 100$ in desilicated solution
		g/liter	g/liter	
1	None used	0	0	0.80
2	1	5	0	.36
3	1	5	50	.14
4	1	5	100	.08
5	1	5	200	.03
6	1	10	0	.19
7	1	10	50	.08
8	1	10	100	.037
9	1	10	200	.004
10	2	10	50	.28
11	3	10	50	.36
12	4	10	50	.11
13	5	10	0	.57
14	5	10	50	.21
15	5	10	100	.10
16	5	10	200	.033
17	6	10	50	.40
18	7	10	50	.12

* (1) Dehydrated kaolin+NaOH+NaCl+H_2O heated in autoclave at 150° C for 4 days.
(2) Undehydrated kaolin+NaOH+NaCl+H_2O heated in autoclave at 150° C for 4 days.
(3) Undehydrated kaolin+Na_2CO_3+NaCl heated in muffle at 820° C for 16 hours.
(4) Preparation (1), above, heated with excess NaCl in muffle at 820° C for 16 hours.
(5) Gibbsite+silica gel+NaOH+NaCl+H_2O heated in autoclave at 150° C for 4 days.
(6) Gibbsite+silica gel+Na_2CO_3+NaCl heated in muffle at 820° C for 16 hours.
(7) Preparation (5), above, heated with excess NaCl in muffle at 820° C for 16 hours.

In these experiments, the quantity of sodium hydroxide or sodium carbonate used was in moderate excess of the amount theoretically required to form sodalite, and the sodium chloride was present in greater excess. As an example of the procedure, a batch of sodalite was prepared by method 1 as follows:

The kaolin was first activated by heating it at 700° C for 1 hour. A batch of 200 g of this dehydrated kaolin, 150 g of NaCl, 100 g of NaOH, and 400 ml of water, was kept at 150° C in an autoclave for 4

days. The product was then removed, washed with hot water, and dried at 110° C. Analysis showed the following composition:

	%
Na_2O	18.32
Al_2O_3	30.47
$Fe_2O_3+TiO_2$	1.67
SiO_2	36.06
NaCl	10.58
H_2O	2.73
Total	99.83

Ignoring the $Fe_2O_3+TiO_2$, this analysis corresponds to the following molar ratios: $0.99Na_2O:1.00Al_2O_3:2.01SiO_2:0.61NaCl:0.51H_2O$, in good agreement with the theoretical molar ratios of sodalite: $1.00Na_2O:1.00Al_2O_3:2.00SiO_2:0.67NaCl$.

To compare the effectiveness of the various sodalite preparations, a large quantity of sodium aluminate solution containing 18.3 g of Al_2O_3 and 0.146 g of SiO_2 per liter was prepared by extraction of sinter R. Various amounts of sodium chloride were dissolved in 400-ml portions of this extract, and these were boiled for 1 hour with the quantities of the various sodalite preparations indicated in table 16.

The results show that the sodalite made by Method 1 is the most active preparation. Comparison of experiments 6 to 9 with 2 to 5 reveals that 10 g of sodalite per liter brought about a more complete desilication than 5 g.

Sodalite prepared in the autoclave from undehydrated kaolin gave poor desilication (experiment 10), and that prepared in the muffle was even less effective (experiment 11). However, when the sodalite obtained by method 1 was heated in the muffle with excess sodium chloride, its desilication capacity was not much impaired (experiment 12).

Experiments 13 to 18, inclusive, show that sodalite prepared from gibbsite and silica gel and the product obtained by method 6 were less active than that prepared from dehydrated kaolin. There was considerable improvement (experiment 18) when the sodalite prepared by method 5 was heated in the muffle at 820° C, method 7.

Comparison of the effectiveness of the various sodalite preparations may be facilitated by reference to figure 14.

For the dilute sodium aluminate solutions obtained in this portion of the investigation, the best conditions for desilication appear to require a concentration of sodium chloride of 200 g/liter and boiling for 1 hour with 10 g of sodalite seed per liter prepared in the autoclave from dehydrated kaolin. Under these conditions the concentration of silica in solution can be reduced to less than 0.01 percent of the alumina concentration.

5. EXTRACTION OF SINTERS WITH CONCENTRATED SODIUM CARBONATE SOLUTIONS

All extractions described in this and following sections were made with high-speed stirring. The extraction mixtures were 100-ml portions of solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride. The quantity of sinter added was such that the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was 2.0. At the end of each extraction the residue was

filtered off and washed with a solution containing the same concentration of sodium chloride as that in the original extraction. A 100-ml portion of this solution was used to wash the residue on the filter. The residue was then subjected to two successive repulpings, for 3 minutes each time, in 200-ml portions of the wash solution. Analyses of the combined extracts and washes were made for Al_2O_3 and also for SiO_2 in some cases.

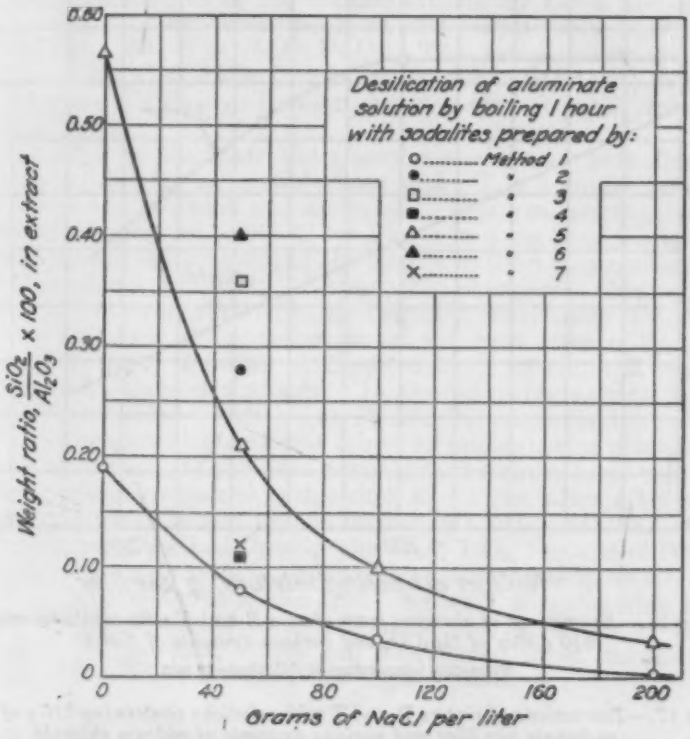

FIGURE 14.—*Comparison of effectiveness of various sodalite preparations (described in table 16) in desilicating an extract, from sinter R, containing 18 g/liter of* Al_2O_3 *and 0.15 g/liter of* SiO_2.

Figure 15 is based on data in table 17 for the 10-minute extractions of the sinters at 70° C. It shows that the extraction of alumina from sinter *R*, though considerably diminished at a sodium chloride concentration of 200 g/liter, is not affected adversely at 100 g of NaCl per liter. The recovery of alumina from sinter T, however, shows an approximately linear decrease as the NaCl concentration increases from 0 to 200 g/liter. Table 17 shows that variations from an extraction time of 10 minutes or temperature of 70° C did not improve the recoveries appreciably. No beneficial results were obtained by prolonged grinding of sinter T.

As mentioned in the preceding section, the dicalcium silicate in sinter T was present as a mixture of the gamma and beta modifications, and grains of the latter were surrounded by glassy films. Sinter R, however, was practically free of beta-dicalcium silicate and glass. It

was thought that the difference in behavior of the sinters might be due in part to these factors, particularly to the presence of the reactive beta-dicalcium silicate in sinter T, which might interfere with the reaction between sodium carbonate and calcium aluminate. Accordingly, an annealing procedure for eliminating glass and beta-dicalcium silicate from the sinter was investigated.

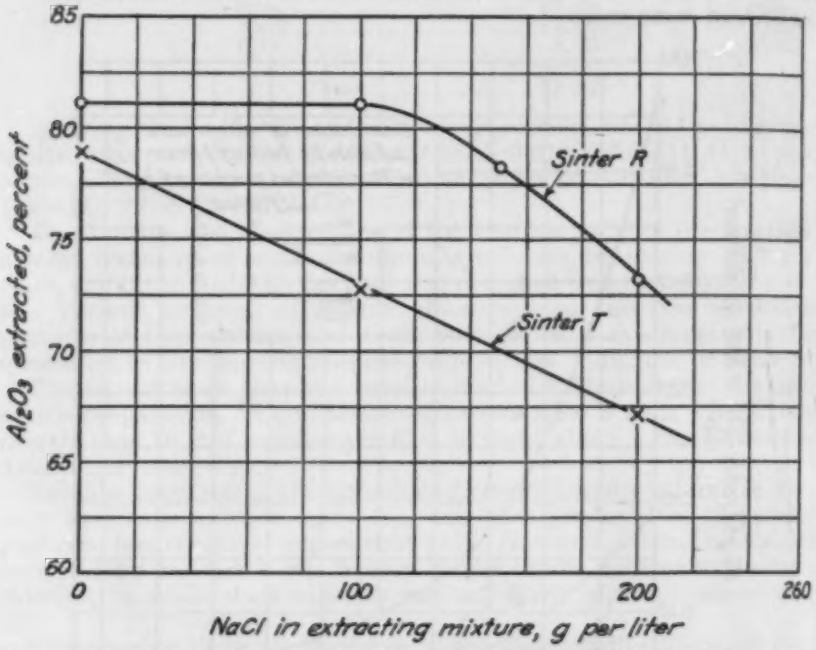

FIGURE 15.—*Extractions of alumina from sinters R and T with solutions containing 210 g/liter of* Na_2CO_3 *and various amounts of* NaCl.

Extraction temperature=70° C; time=10 min

TABLE 17.—*Extractions of sinters* R *and* T *with solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter=2.0. High-speed stirring.]

Experiment	Sinter	Quantity of sinter extracted	NaCl in extracting solution	Temperature of extraction	Time of extraction	Al_2O_3 recovery
		g/liter	g/liter	° C	min	%
1	R	550	0	70	10	81.1
2	R	550	100	70	10	81.0
3	R	550	100	70	15	81.5
4	R	550	100	70	20	79.3
5	R	550	150	70	10	78.3
6	R	550	200	70	10	73.1
7	T	561	0	70	10	78.9
8	T	561	100	70	5	72.0
9	T	561	100	70	10	73.7
10	T	561	200	70	10	67.0
11	T	561	200	70	30	66.1
12	T	561	200	40	10	61.5
13	T	561	0	80	5	78.3
14	T	561	100	80	5	74.5
15	T	561	100	90	5	78.4

6. ANNEALING OF SINTERS

Lerch and coworkers [15] have shown that complete crystallization of cement clinkers may be induced by heating them to 1,400° C and allowing the temperature to drop slowly to a value below the solidus in the system. Such "annealed" products were found to be practically free from glass and to contain dicalcium silicate exclusively in the gamma form.

The alumina content of the clinkers studied by Lerch and Brownmiller [15] was distributed between the compounds $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$. The temperature of liquid formation when $CaO.Al_2O_3$ is substituted for $3CaO.Al_2O_3$, as in the sinters studied in this investigation, is unknown but in all probability is above 1,200° C.

Accordingly, to eliminate the glassy material and beta-dicalcium silicate as completely as possible from sinter T, a 3-pound sample of the material was reheated and annealed. This was accomplished by reburning the sinter at 1,300° C for 1 hour in a gas-fired furnace and then causing the temperature of the charge to drop at a uniform rate to 1,200° C over a period of 1½ hours. The charge was then removed from the furnace and allowed to cool rapidly, whereupon it "dusted" completely because of the inversion of the beta form of dicalcium silicate to the gamma form. A 3-pound batch of sinter R was also reburned and annealed similarly. In the following section the annealed sinters will be designated as R_a and T_a, respectively.

Another portion of sinter T was reburned and annealed after adjusting its composition. It had been noted that this sinter had a relatively low lime content compared with sinter R. Thus, after allowing for the lime and alumina required to form $2CaO.SiO_2$, $CaO.TiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and $Na_2O.Al_2O_3$ with the SiO_2, TiO_2, Fe_2O_3, and Na_2O in the sinters, the molar ratio of residual lime to alumina in sinter T was 1.15, whereas in sinter R it was 1.30. Sinter T was therefore mixed with 2 percent of added lime, reburned, and annealed as before. Analysis of the product, which will be referred to in the following section as sinter T'_a, gave the following composition:

	%
SiO_2	22.14
Al_2O_3	17.69
Fe_2O_3	1.28
TiO_2	0.93
CaO	56.06
MgO	0.93
Na_2O	.64
Loss on ignition	.23
Total	99.90

All of the annealed sinters were extremely fine-grained and passed completely through a No. 200 sieve. Petrographic examinations indicated that they were free of glass and beta-dicalcium silicate.

7. EXTRACTION OF ANNEALED SINTERS WITH CONCENTRATED SODIUM CARBONATE SOLUTIONS

Samples of sinter T_a, which had been annealed without adjustment of composition, were extracted at 70° and 80° C with solutions containing 210 g of Na_2CO_3 per liter, with and without added NaCl.

Table 18 shows that the extractions were better than those made on the original sinter (table 17), but they were still unsatisfactory in the presence of NaCl.

TABLE 18.—*Extraction of annealed sinter T_a with solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter=2.0. Weight of sinter per liter of extracting solution=561 g. High-speed stirring]

Experiment	NaCl in extracting solution	Temperature of extraction	Time of extraction	Al_2O_3 recovery
	g/liter	*° C*	*min*	*%*
1	0	70	20	82.7
2	100	70	10	76.5
3	100	70	20	76.7
4	0	80	10	78.6
5	100	80	10	76.0

However, annealing caused a considerable improvement in extractions of alumina at 70° C from sinter R_a, as shown by comparison of tables 17 and 19. A corresponding improvement resulted from the annealing of sinter T'_a. Furthermore, the extractions of alumina from both sinters were not seriously affected by high concentrations of sodium chloride when the molar ratio of sodium carbonate in the solutions to alumina in the sinters was increased from 2.0 to 2.5.

The extractions shown in table 19 were unexpectedly large, especially for sinter R_a, which even before annealing contained very little beta-dicalcium silicate and glass. It is known, however, that dicalcium silicate forms extensive solid solutions with various oxides, and a possible cause of the increased extractions might be the elimination of calcium aluminate from solid solution in dicalcium silicate. Such ex-solution would be favored by annealing. Rankin and Wright in

TABLE 19.—*Extractions at 70° C of annealed sinters, R_a and T'_a, with solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[High-speed stirring]

Experiment	Sinter	Quantity of sinter extracted	Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter	NaCl in extracting solution	Time of extraction	Al_2O_3 recovery	$\frac{SiO_2}{Al_2O_3}\times 100$ in solution
		g/liter		*g/liter*	*min*	*%*	
1	R_a	550	2.0	0	10	93.5	2.6
2	R_a	550	2.0	100	10	89.6	1.9
3	R_a	550	2.0	200	10	83.9	1.8
4	T'_a	571	2.0	0	10	90.2	2.6
5	T'_a	571	2.0	100	10	86.6	2.1
6	T'_a	571	2.0	200	10	81.0	1.5
7	R_a	440	2.5	0	10	92.9	2.8
8	R_a	440	2.5	100	10	92.4	1.9
9	R_a	440	2.5	200	10	90.4	1.3
10	R_a	440	2.5	200	20	90.2	1.9
11	R_a	440	2.5	200	30	92.9	1.5
12	T'_a	457	2.5	0	10	94.6	2.9
13	T'_a	457	2.5	100	10	94.4	1.9
14	T'_a	457	2.5	200	10	92.9	1.9
15	T'_a	457	2.5	200	20	93.2	1.2
16	T'_a	457	2.5	200	30	89.8	1.1

TABLE 20.—*Compositions of extracts and washes from extractions of annealed sinters, with solutions containing 210 g of sodium carbonate per liter and various amounts of sodium chloride*

[High-speed stirring]

Experiment	Sinter	Quantity of sinter extracted	Extracting solution: Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter	Extracting solution: NaCl content	Temperature of extraction	Time of extraction	Extract: Volume	Extract: Al_2O_3 content	Extract: $\frac{SiO_2}{Al_2O_3}\times 100$	Wash: Al_2O_3 content	Wash: $\frac{SiO_2}{Al_2O_3}\times 100$	First repulp: Al_2O_3 content	First repulp: $\frac{SiO_2}{Al_2O_3}\times 100$	Second repulp: Al_2O_3 content	Second repulp: $\frac{SiO_2}{Al_2O_3}\times 100$	Third repulp: Al_2O_3 content	Third repulp: $\frac{SiO_2}{Al_2O_3}\times 100$	Overall Al_2O_3 extraction	Overall $\frac{SiO_2}{Al_2O_3}\times 100$ in solution
		g/liter		*g/liter*	*°C*	*min*	*ml*	*g/liter*		*g*		*g*		*g*		*g*		%	
1	R_a	440	2.5	0	70	30	58	93	4.35	2.29	3.82	0.071	6.7	0.019	8.1			95.2	4.23
2	R_a	440	2.5	100	70	10	67	55	2.45	2.01	1.74	.800	0.90	.194	0.26	0.101	1.3	84.3	1.97
3	R_a	440	2.5	100	70	20	65	65	2.71	2.20	2.46	.652	.94	.206	.20	.104	1.3	91.2	2.39
4	R_a	440	2.5	100	70	30	51	84	3.30	2.72	2.93	.554	1.32	.174	.86	.045	3.3	96.0	2.98
5	R_a	440	2.5	150	70	10	67	63	2.43	2.20	2.12	.536	0.80	.584	.50	.096	1.1	94.9	2.07
6	R_a	440	2.5	150	70	20	58	73	2.59	2.52	2.31	.370	1.22	.606	.63	.190	0.74	97.5	2.23
7	R_a	440	2.5	150	70	30	50	82	2.78	2.64	2.44	.432	0.95	.700	.57	.214	.56	98.2	2.34
8	R_a	440	2.5	200	70	10	64	58	1.79	2.14	1.65	.548	.40	1.000	.40			89.7	1.49
9	R_a	440	2.5	200	70	20	58	67	2.10	2.55	1.80	.380	.95	0.585	.51			90.7	1.80
10	R_a	440	2.5	200	70	30	56	65	2.17	2.66	1.83	.842	1.09	.360	.70	.168	.71	93.9	1.83
11	T'_a	457	2.5	0	70	30	46	92	3.84	3.22	2.73	.268	7.8	.024	31.0	.008	46.0	95.8	3.64
12	T'_a	457	2.5	100	70	30	54	71	3.02	2.45	2.57	.994	1.13	.148	0.20	.032	1.2	92.4	2.56
13	T'_a	457	2.5	150	70	20	62	60	2.27	2.23	2.11	.730	0.70	.424	.45	.166	0.84	89.7	1.92
14	T'_a	457	2.5	150	70	30	52	71	2.70	2.50	2.32	.780	.76	.608	.62	.087	1.0	94.3	2.19
15	T'_a	457	2.5	200	70	10	64	55	2.02	1.92	1.98	.418	.62	1.174	.42			87.6	1.64
16	T'_a	457	2.5	200	70	20	65	58	2.06	1.98	1.82	.374	1.04	1.045	.42			89.5	1.70
17	T'_a	457	2.5	200	70	30	54	67	2.22	2.13	2.04	.468	1.03	0.974	.44			90.2	1.94
18	T'_a	457	2.5	150	80	30	40	80	2.47	2.72	2.61	.568	0.92	1.084	.44	.131	1.1	95.4	2.10
19	T'_a	457	2.5	150	90	30	24	90	2.92	3.26	2.45	2.262	.72	0.330	.76	.041	1.5	99.8	2.02
20	T'_a	507	2.25	100	70	30	45	78	3.13	3.29	2.81	1.182	.81	.202	.24	.084	1.8	92.2	2.55
21	T'_a	507	2.25	150	70	30	54	70	2.69	2.67	2.34	1.128	.76	.484	.17	.070	1.0	90.4	2.14

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their study of the system $CaO–Al_2O_3–SiO_2$ [16] were not able to detect solid solution of aluminates in dicalcium silicate, but Green [17] has shown that in the more complex systems containing Fe_2O_3, Na_2O, etc., the occurrence of rather extensive solid solution of alumina-bearing compounds in dicalcium silicate is possible.

To ascertain the distribution of alumina between the extracts from the sinters and successive washings of the residues, the experiments listed in table 20 were performed. Each extraction was made with

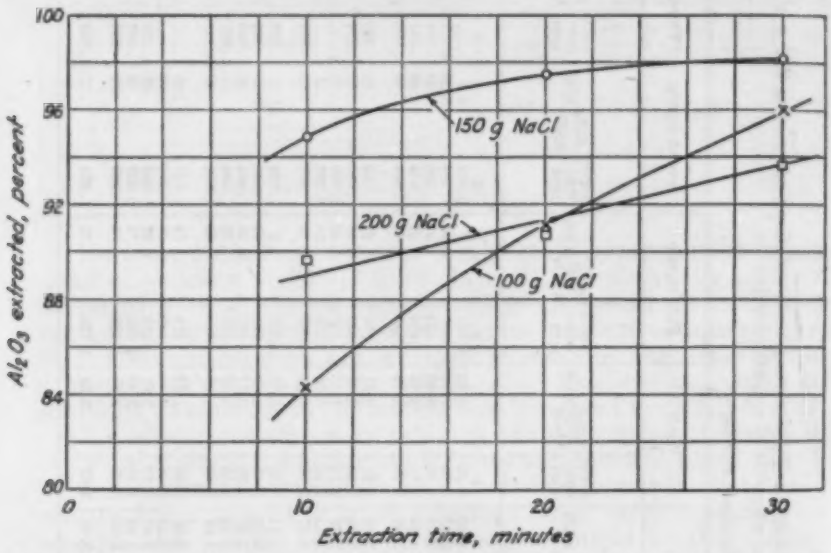

FIGURE 16.—*Rate of extraction at 70° C of alumina from sinter R_a (i. e., sinter R after annealing) with solutions containing 210 g/liter of Na_2CO_3 and various amounts of* NaCl.

a 100-ml portion of a solution containing 210 g of Na_2CO_3 per liter and the indicated amounts of NaCl. After removal of the extract by filtration, the residue was washed with a solution containing the same concentration of sodium chloride as that in the original extraction. The residue was washed with a 100-ml portion of the solution and then was repulped two or three times, for 3 minutes each time, in 200-ml portions of the wash solution. The four or five filtrates thus obtained in each experiment were analyzed separately for SiO_2 and Al_2O_3.

Figure 16 shows the rate of extraction of alumina from sinter R_a at various concentrations of sodium chloride in the extracting solutions. The best extractions at 10, 20, and 30 minutes were obtained when the sodium chloride concentration was 150 g/liter. At 100 g of NaCl per liter a longer extraction period than 30 minutes is apparently necessary. Figure 17 permits comparisons of the effects of various concentrations of sodium chloride on the 30 minute extractions. A concentration of 150 g of NaCl per liter appears to be the optimum, and above this a marked decrease in extraction occurs. As shown in this figure, the quantity of SiO_2 in the extracts decreases linearly with increase in the NaCl concentration of the solutions.

Extraction of sinter R_a with Na_2CO_3-NaCl solution of suitable concentration thus has a twofold advantage over extraction with Na_2CO_3 solution alone, in increasing the quantity of Al_2O_3 dissolved and decreasing that of SiO_2. If it is assumed that SiO_2 and Al_2O_3 will be removed from solution in approximately equal percentages during desilication, the net recoveries of alumina in experiments 1 (no NaCl) and 7 (150 g of NaCl per liter), table 20, will be 91 and 96 percent, respectively.

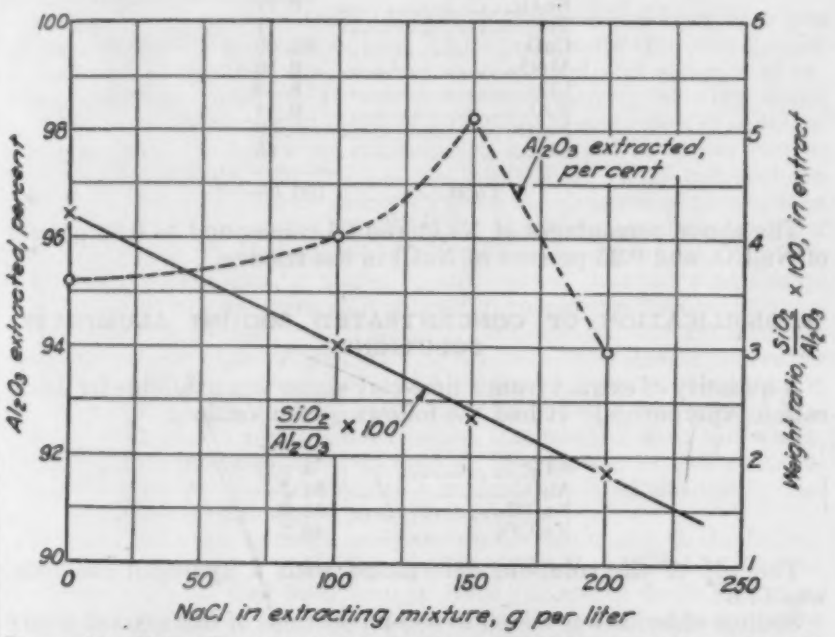

FIGURE 17.—*Effect of sodium chloride on recovery of* Al_2O_3 *and on silica-alumina ratio in extracts from sinter* R_a.

Initial solutions contain 210 g/liter of Na_2CO_3 and various amounts of NaCl. Extraction temperature=70° C; time=10 min.

A slight disadvantage of the use of sodium chloride is the reduction it causes in the Al_2O_3 contents of the extracts. Thus, with 0 and 150 g of NaCl per liter in the initial solutions, the concentrations of Al_2O_3 in the extracts from sinter R_a are 93 and 82 g of Al_2O_3 per liter, respectively. The corresponding values for sinter T'_a are 92 and 71 g of Al_2O_3 per liter, respectively.

The extractions of Al_2O_3 from sinters R_a and T'_a are practically identical in the absence of NaCl, but most of the extractions of sinter T'_a with Na_2CO_3-NaCl solutions are several percent less than those of sinter R_a. In order to determine the effect of increased temperature, extractions of sinter T'_a were made at 80° and 90° C (experiments 18 and 19). At 90° C practically all the Al_2O_3 in the sinter was obtained in solution. The volumes of the extracts obtained at the higher temperatures were considerably less than those at 70° C.

Extractions 20 and 21 were made using a molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter of 2.25 instead of 2.5. Comparison of

corresponding extractions shows that the lower molar ratio is satisfactory at 100 g of NaCl per liter in the initial solution but not at 150 g of NaCl per liter.

An analysis was made of the residue from extraction 4 after washing with hot water and drying at 110° C. The following values were obtained:

	%
SiO_2	24.77
Al_2O_3	1.01
Fe_2O_3	0.77
TiO_2	.71
CaO	62.69
MgO	0.50
CO_2	8.72
H_2O	0.44
Na_2O	.33
Cl	.15
Total	100.09

The above percentages of Na_2O and Cl correspond to 0.34 percent of Na_2CO_3 and 0.25 percent of NaCl in the residue.

8. DESILICATION OF CONCENTRATED SODIUM ALUMINATE SOLUTIONS

A quantity of extract from a lime-clay sinter was available for desilication experiments. It had the following composition:

	g/liter
SiO_2	3.015
Al_2O_3	84.7
NaOH	101.9
Na_2CO_3	40.2

The pH of the solution, determined with a hydrogen electrode, was 13.64.

Sodium chloride was added to 500-ml portions of this extract to give 100, 150, and 200 g of NaCl per liter of solution. These portions and like volumes of the original extract were placed in iron containers fitted with reflux condensers and each solution was boiled for 2 hours with various amounts of synthetic sodalite prepared from dehydrated kaolin. Analyses of the resulting solutions for SiO_2 and Al_2O_3 gave the values shown in table 21.

TABLE 21.—*Desilication of concentrated sodium aluminate extract containing various amounts of sodium chloride, by boiling for 2 hr with synthetic sodalite*

Experiment	NaCl in solution	Sodalite added as seed	Composition of solution after desilication		
			SiO_2	Al_2O_3	$\frac{SiO_2}{Al_2O_3}\times 100$
	g/liter	*g/liter*	*g/liter*	*g/liter*	
1	0	10	0.344	81.4	0.42
2	100	10	.221	81.1	.27
3	150	10	.220	81.1	.27
4	200	0	.371	80.7	.46
5	200	10	.139	80.9	.17
6	200	30	.081	81.0	.10
7	200	50	.040	80.9	.05

Although the desilication improved as the sodium chloride concentration increased, undesirably large amounts of silica remained dissolved when the quantity of seed used was 10 g/liter of solution. It was thought that this amount of seed might be insufficient in view of the large amount of silica in the extract. To eliminate the silica completely from 500 ml of solution would require the precipitation of 8.1 g of sodalite. Accordingly, the amount of seed was increased to 20 and 50 g/liter in experiments 6 and 7, respectively, and improved desilications were obtained.

In experiment 4, the extract containing 200 g of NaCl per liter was boiled without the addition of seed. The precipitate that was formed was separated by filtration, washed with alcohol and ether, and examined microscopically. It was composed entirely of very small isotropic crystals having an index of refraction close to that of sodalite. Analysis gave the following composition expressed in molar ratios: $1.03\ Na_2O{:}1.00Al_2O_3{:}1.67SiO_2{:}0.23NaCl{:}3.06H_2O$. The composition of this precipitate differs considerably from the theoretical proportions of sodalite, $Na_2O.Al_2O_3.2SiO_2.0.67NaCl$. If the material precipitated in the presence of seed shows a corresponding departure from the composition of sodalite, it might be anticipated that the seed charge would become less effective as it is used in successive desilications.

To determine whether such deterioration occurs, the experiments recorded in table 22 were carried out. The same desilication procedure as before was followed, using 500-ml portions of the extract containing 100 g of NaCl. In the first cycle, 25 g of sodalite was used. The sodalite recovered after this desilication was washed with hot water, alcohol, and ether, and dried in air. A 25-g charge of this material was then used for desilication of a second batch of solution. The same procedure was repeated in a third desilication.

The original sodalite had a composition corresponding to the following molar ratios: $0.99Na_2O{:}1.00Al_2O_3{:}2.01SiO_2{:}0.61NaCl{:}0.54H_2O$. After this material had been used in three successive desilications, as indicated in table 22, it was reanalyzed and the following molar ratios obtained: $1.00Na_2O{:}1.00Al_2O_3{:}2.04SiO_2{:}0.56NaCl{:}1.96H_2O$. Thus, it appears that the material precipitated in the presence of seed has very nearly the theoretical composition of sodalite. However, a slight decrease in NaCl content and increase in water of hydration of the mixture of seed and precipitate had occurred.

It seemed possible that the sodium chloride content of the sodalite, and also its desilication efficiency, might be restored by treating the

TABLE 22.—*Effectiveness of sodalite on repeated use for desilicating a concentrated sodium aluminate solution (cycles 1, 2, and 3), and the subsequent improvement caused by boiling the used sodalite for 2 hr with a solution saturated with* NaCl *(cycle 4)*

[Volume of sodium aluminate solution, containing 100 g of NaCl, 500 ml; quantity of sodalite, 25 g; time of boiling, 2 hr.]

Cycle	$\frac{SiO_2}{Al_2O_3}\times 100$ in desilicated solution
1	0.053
2	.067
3	.080
4	.057

used preparation with sodium chloride solution. Accordingly, the seed charge recovered from cycle 3, table 22, was boiled for 2 hours with a saturated salt solution, and 25 g of this product was used to desilicate another batch of extract. As shown in table 22, the seed charge than gave a more effective desilication than the original sodalite.

The desilications recorded in table 23 were made on duplicates of extracts, having the same numbers, listed in table 20. These extracts, in volumes of 120 to 150 ml, were boiled with synthetic sodalite, in the proportion of 25 g/liter of solution. It was found to be advantageous to disperse the sodalite in the extracts by high-speed stirring before boiling.

All of the desilicated extracts (table 23) are sufficiently low in silica and high in alumina to permit differential precipitation of alumina containing about 0.02 percent of silica, according to the method described by McCulloch [7].

TABLE 23.—*Desilication of extracts from sinters R_a and T'_a, by boiling with synthetic sodalite*

[Sodalite, 25 g/liter]

Experiment	Sinter	NaCl in extracting solution	Al_2O_3 in extract	Time of boiling for desilication	$\frac{SiO_2}{Al_2O_3} \times 100$ in extract	
					Before desilication	After desilication
		g/liter	g/liter	hr		
4	R_a	100	84	2	3.30	0.10
7	R_a	150	82	1	2.78	.082
7	R_a	150	82	2	2.78	.077
10	R_a	200	65	2	2.17	.057
12	T'_a	100	71	1	3.02	.15
14	T'_a	150	71	1	2.70	.035
16	T'_a	200	58	2	2.06	.060

9. THEORY OF SODALITE DESILICATION

It has been shown that desilication of a sodium aluminate solution is favored by the following factors: (1) The presence of a high concentration of sodium chloride in the solution, (2) the presence or formation of a seed charge of sodalite, (3) a boiling temperature at atmospheric pressure or higher temperatures and pressures, and (4) sufficient time for precipitation of sodalite to approach completion.

In the initial extraction of the lime-clay sinters, the above conditions must be avoided, insofar as possible, to prevent losses of soda and alumina that would result from formation of sodalite at this stage. Because economical operation of the process requires a high concentration of sodium chloride in the extracting solution, the precipitation of sodalite is prevented by using a short extraction time at a temperature below boiling, and with the exclusion of material that might serve as seed.

Sodalite liberates sodium chloride to solution when in contact with boiling water [6] and thus is incongruently soluble. The end product resulting from complete liberation of the sodium chloride in sodalite is probably the comparatively soluble hydrated sodium aluminum silicate formed in the Bayer process. At high concentrations of sodium chloride in solution, the solubility of sodalite becomes increas-

ingly congruent and diminishes to very low values. Sodium hydroxide, however, has an effect opposite to that of sodium chloride, and sodalite becomes less stable as the alkalinity of the solution rises.

The function of the seed charge during desilication is to induce the precipitation of crystalline sodalite. As shown in the preceding section, the material precipitated from solution in the absence of seed has a composition differing considerably from that of sodalite but, when seed is present, the precipitate has very nearly the theoretical composition.

10. FLOW SHEET AND SUMMARY OF PROCESS

A suggested commercial process for the extraction of alumina from clay, by the lime-sinter method developed in this study, is shown in figure 18.

The composition of the clay given in the flow sheet is that of a kaolin used in this investigation. Minor constituents of the kaolin are omitted in order to simplify the diagram. A mixture of clay and limestone is prepared by either wet or dry process grinding and mixing. The composition of the resulting material on an ignited basis should correspond approximately to a point on the line joining $2CaO.SiO_2$ and the quintuple point $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $2CaO.SiO_2$ in the CaO-Al_2O_3-SiO_2 diagram. Allowance is made for the lime and alumina required for the formation of $CaO.TiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, or $Na_2O.Al_2O_3$ with any TiO_2, Fe_2O_3, or Na_2O in the raw materials.

The equipment described by McLarmour, McMaster, and Jacques [18] appears to be particularly well adapted for burning the raw mix and annealing the resulting clinker. This apparatus consists of an ordinary rotary kiln in series with a rotary cooler carrying a burner installed at its feed end. The clinker discharged from the primary kiln can be annealed in the cooler at a rate determined by its speed of rotation and by adjustment of the burner.

Complete dusting of the annealed clinker obviates the need of grinding. The material is extracted for about one-half hour at 60 to 80° C with a solution containing approximately 200 g of Na_2CO_3 and 150 g of NaCl per liter. High-speed stirring of the slurry is used.

On completion of the extraction period, the mixture is filtered and an extract containing 70 to 80 g of Al_2O_3 and 1 to 2 g of SiO_2 per liter is obtained. By subjecting the residue to counter-current washing with salt solution, it is anticipated that the concentration of Al_2O_3 in the wash water can be built up to approach that in the extract. The residue may then be washed with water and stock-piled as a raw material for the manufacture of portland cement.

The solution, plus concentrated washings, is next desilicated by boiling it for 1 hour with a seed charge of synthetic sodalite (25 g/liter of solution). After filtration, the sodalite in excess of that required for seed for the next batch is returned to the first stage of the process, allowance for its addition being made in calculation of the amount of limestone to be used in the subsequent batch. By this means, the alumina and soda in the excess sodalite are recovered.

Alumina is precipitated as gibbsite by passing carbon dioxide into the desilicated solution. Scrubbed gases from the kiln are the source of carbon dioxide. In order to avoid contamination by silica, the precipitation of alumina is not carried to completion. However, in

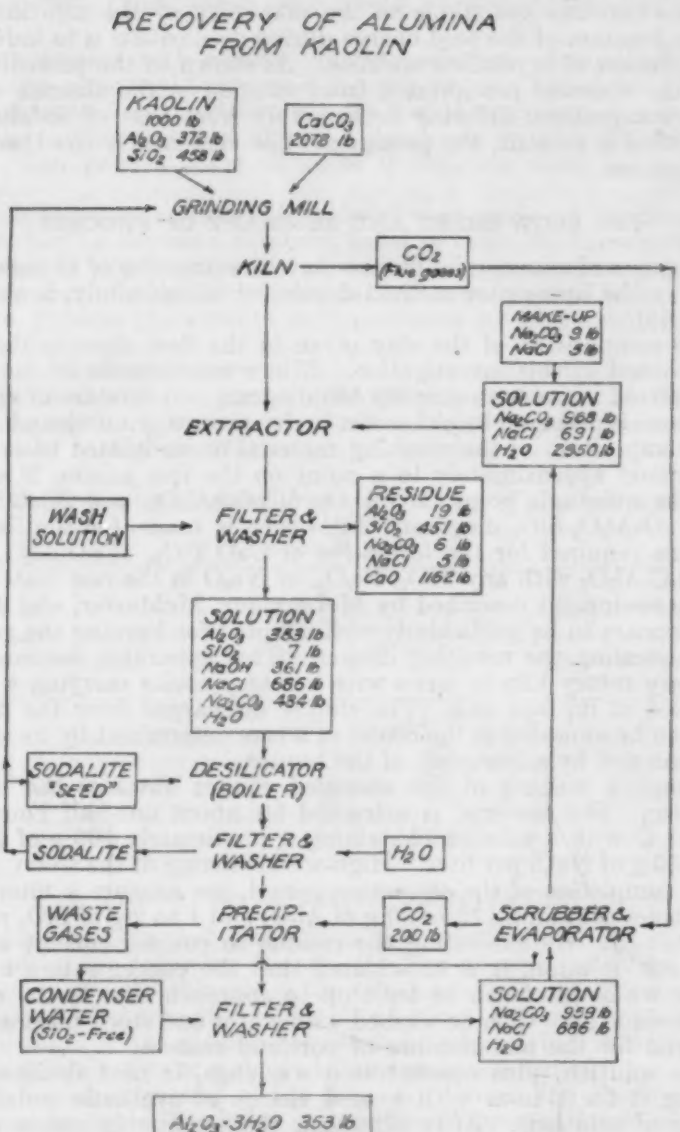
RECOVERY OF ALUMINA FROM KAOLIN
KAOLIN 1000 lb Al2O3 372 lb SiO2 458 lb
CaCO3 2078 lb
GRINDING MILL
KILN
CO2 (Flue gases)
MAKE-UP Na2CO3 9 lb NaCl 3 lb
SOLUTION Na2CO3 569 lb NaCl 691 lb H2O 2950 lb
EXTRACTOR
WASH SOLUTION
FILTER & WASHER
RESIDUE Al2O3 19 lb SiO2 451 lb Na2CO3 6 lb NaCl 5 lb CaO 1162 lb
SOLUTION Al2O3 383 lb SiO2 7 lb NaOH 361 lb NaCl 686 lb Na2CO3 434 lb H2O
SODALITE "SEED"
DESILICATOR (BOILER)
SODALITE
FILTER & WASHER
H2O
WASTE GASES
PRECIP-ITATOR
CO2 200 lb
SCRUBBER & EVAPORATOR
CONDENSER WATER (SiO2-Free)
FILTER & WASHER
SOLUTION Na2CO3 959 lb NaCl 686 lb H2O
Al2O3·3H2O 353 lb SiO2 0.05 lb Na2CO3 3 lb 95% RECOVERY SiO2/Al2O3 = 0.02%

FIGURE 18.—*Flow sheet of suggested process for extracting alumina from kaolin.*

cyclical operation of the process, complete recovery of the alumina from solution would be obtained and this is indicated in the flow sheet. The hydrated alumina is filtered and washed with water, low in silica to avoid contamination. The residual solution and the washings are used to scrub the kiln-flue gases. This procedure effects evaporation of water from the combined solution and washings, and dust is removed from the gases. Make-up quantities of sodium carbonate and sodium chloride are added to the evaporated and carbonated solution, which is then used for extraction of a fresh batch of sinter. The precipitated gibbsite is dried and calcined for electrolytic reduction to aluminum.

IV. EXTRACTION OF ALUMINA FROM HIGH-SILICA BAUXITES BY THE LIME-SINTER PROCESS

1. MATERIALS

Bauxite B, the composition of which is given in table 1, was selected for study. Other experiments were made on a diaspore bauxite (bauxite E) having the following composition:

	%
SiO_2	18.16
Al_2O_3	50.62
Fe_2O_3	11.37
TiO_2	3.23
CaO	0.00
MgO	.04
Na_2O	.07
Loss on ignition	16.27
Total	99.76

The major part of the iron oxide content of this material was in the ferrous state, as siderite.

Other materials included calcium carbonate, sodium carbonate, sodium chloride, and sodium hydroxide.

2. PROCEDURE, RESULTS, AND DISCUSSION

Calcium carbonate-bauxite mixtures were prepared which, after burning, would contain Al_2O_3 as $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$; SiO_2 as $2CaO.SiO_2$; and TiO_2 as $CaO.TiO_2$. The mixture made from bauxite B, in 100-g batches, was heated in an electric furnace at 1,300° C for 1 hour and cooled slowly, but without careful control of annealing temperatures. Complete dusting of the product occurred on cooling.

Extractions were made of the dusted sinter at 50° C for 2 hours, using a slow-speed shaking machine. Table 24 shows the recoveries of Al_2O_3 obtained after desilication of the extracts with sodalite. The highest extraction was obtained when the molar ratio of Na_2CO_3 in solution to Al_2O_3 in the sinter was 4.0. Small amounts of NaOH in the initial solutions had little effect on the extractions, but a concentration of 50 g of NaOH per liter (experiment 4) gave a greatly reduced recovery of Al_2O_3.

A sample of sinter B was reheated to 1,300° C, in an electric furnace, held at that temperature for 1 hour, and cooled to 1,150° C at a uniform rate of 1 degree per minute. The dusted sinter was ex-

tracted for ½ hour at 70° C with a solution containing 50 g of Na_2CO_3 and 150 g of NaCl per liter, using high-speed stirring. The residue was washed by the multiple repulping procedure described previously. An over-all recovery of 97 percent of the Al_2O_3 in this sinter was obtained in solution and the over-all SiO_2 was 1.22 percent. The recovery of Al_2O_3 is approximately the same as those obtained from sinters R_a and T'_a under corresponding conditions.

A 3-pound batch of the mixture of calcium carbonate and bauxite E was burned in a gas-fired furnace at 1,300° C for 1 hour and cooled to 1,200° C in 1½ hours. The product, which failed to dust, was ground to pass a No. 200 sieve. Only 71 percent of the alumina in this sinter was obtained in solution by the procedure given in the preceding paragraph.

TABLE 24.—*Extraction at 50° C of lime sinter prepared from bauxite B (84.6 g of sinter per liter of extracting solution)*

[Time of extraction, 2 hr]

Experiment	Composition of extracting solution			Molar ratio of Na_2CO_3 in solution to Al_2O_3 in sinter	Al_2O_3 on recovery	$\frac{SiO_2}{Al_2O_3} \times 100$ in solution
	Na_2CO_3	NaOH	NaCl			
	g/liter	g/liter	g/liter		%	
1	38	5	136	1.5	76	0.03
2	50	0	179	2.0	80	.07
3	99	5	317	4.0	84	.04
4	38	50	207	1.5	25	.09

To compare the behavior of the lime sinters of bauxites B and E, parallel experiments were made in which samples of the raw mixes were heated to 1,300° C in an electric furnace, held at that temperature for 1 hour, and cooled to 1,150° C at the rate of 2 degrees per minute. The sinter from bauxite B dusted completely, but that from bauxite E failed to dust. As both sinters contained approximately the same amount of Fe_2O_3, the difference in behavior was attributed to the presence of about 37 percent of dicalcium silicate in the bauxite B sinter as compared with 30 percent in that of bauxite E.

It was concluded that bauxite E would have to be mixed with a material of higher silica content to obtain a sinter that would dust satisfactorily. For this purpose a mixture of 75 percent of bauxite E and 25 percent of kaolin (based on ignited weights) was prepared. A sample was heated in an electric furnace to 1,300° C, held at that temperature for 1 hour, and cooled to 1,150° C at 1 degree per minute. The product, which contained about 41 percent of dicalcium silicate, dusted completely. Extractions, made as before, dissolved 88 percent of the Al_2O_3 from the sinter.

It is not known why the extractions of the bauxite E sinters are inferior to those of bauxite B. Analysis of bauxite E for P_2O_5 and Cr_2O_3 showed only traces of these oxides, which, in small amounts, might prevent the complete beta-gamma inversion of dicalcium silicate.

The above experiments appear to indicate that the suitability of an aluminous ore, as a raw material for the extraction of alumina by the lime-sinter method, cannot be accurately predicted without actual laboratory tests. This is because of the numerous factors

which affect the completeness of the beta-gamma inversion of dicalcium silicate, on which the success of the method depends. In general, it appears that annealing must be the more prolonged, the higher the proportion of fluxing oxides in the sinter and the lower the dicalcium silicate content. Sinters containing as little as 20 percent of dicalcium silicate can be made to dust, as shown by Lerch and Brownmiller [15], but a 17-hour annealing schedule was required.

V. POSSIBLE COMMERCIAL SIGNIFICANCE OF METHODS

The principal advantage of preparing sodium aluminate solutions by the method described in section II consists in the attainment of a more complete separation of alumina and silica than is given by the Bayer process. This fact makes it possible to precipitate a considerably greater proportion of alumina from the salt-containing extract than from the Bayer solution, before contamination of the precipitated alumina by silica becomes excessive.

In the recovery of soda and alumina from the "red-mud" residues, the use of an extracting solution containing sodium chloride permits the subsequent desilication to be carried out at atmospheric pressure rather than in autoclaves as has been the practice heretofore.

It is believed that the lime-sinter process developed in this study has considerable commercial promise, particularly as applied to clay, for the following reasons:

1. Recoveries of approximately 95 percent of the alumina in clay can be obtained from annealed lime-clay sinters. Such recoveries are comparable with those obtained by acid extraction of kaolin clays [10] and exceed values that have been reported for other alkaline processes [5].
2. Losses of alkali are small.
3. All steps of the process can be carried out at atmospheric pressure.
4. As shown in the flow sheet, the process is simple and no unusual equipment is required.

In common with other alkaline methods for the extraction of alumina from clay, this process suffers from the disadvantage of requiring calcination of the clay with somewhat more than twice its weight of limestone. Only large-scale operation will show whether the cost of this step will be sufficiently compensated by the factors listed above.

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STABILITY OF DOUBLE-WALLED MANGANIN RESISTORS

By James L. Thomas

ABSTRACT

The international ohm is now maintained at the National Bureau of Standards by means of double-walled manganin resistors. It is assumed that the average resistance of a group of 10 standards, selected from a group of 24 constructed in 1933, remains constant with time. No one of the 10 standards has changed in resistance with reference to their average by more than 1 part in a million in 12 years.

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I. INTRODUCTION

Although the international ohm is defined in terms of the resistance of a column of mercury, wire-wound standards are used at national standardizing laboratories for maintenance of the unit of resistance. At the National Bureau of Standards the international ohm is maintained by means of a group of 1-ohm resistors. From this group 10 standards have been selected, and the assumption is made that the average of their resistances remains constant with time. If there is a relatively large change in the resistance of one standard with reference to the average, it is replaced with one that has remained constant. In this way standards are eliminated from the reference group when they become defective.

Values of resistance were originally assigned to standards of the reference group in terms of mercury-ohm determinations made in England and in Germany before 1910. Mercury-ohm determinations were made at this Bureau in 1911 and 1912, and the results were consistent with the English and German results to 15 or 20 parts in a million.[1] In 1910 the reference group consisted of 1-ohm standards of the type developed by Rosa,[2] and resistors of that group were used for over 25 years. Starting in 1931 the standards of the Rosa type were gradually replaced by standards of the double-walled type.[3] Since 1939, maintenance of the international ohm has been entirely by means of a new group of double-walled resistors constructed in 1933. Resistors of the later group have been far superior to any others made at this Bureau, and, judged on the basis of relative stability, are about one order better than well-aged standards of the Rosa type. It is the purpose of this paper to describe the new standards and give a report of their performance to date.

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II. DESCRIPTION OF NEW RESISTORS

The standards constructed in 1933 consisted of a group of 24 of the double-walled type, and the same technic was used for annealing and mounting as that described in Research Paper RP201. The containers, however, were larger than those of the original double-walled group, and were similar in size and general appearance to O. Wolff's model IV.

The increase in the size of the containers made possible the use of larger resistance wire, thus decreasing the ratio of area to volume and thereby reducing possible changes in resistance from surface changes. The resistance coils were made of 28 turns of No. 12 AWG manganin wire (2.05 mm=0.081 in.) from two lots of specially selected wire,[4] wound on 8-cm mandrils and spaced with copper wire. Before the wire was annealed, it had a slightly negative temperature coefficient of resistance at 25° C, and after being annealed, the coefficients were very small, averaging 1 part in a million per degree centigrade for the 24 standards, the maximum coefficient being 3.05 ppm per degree centigrade.

For annealing the resistance coils, a special furnace was constructed, using a fuzed-quartz tube about 10 cm in diameter and 75 cm in length. This tube was sealed at one end, and the other end was covered with a ground-glass plate through which were sealed thermocouple leads and an exhaust tube. Several parallel aluminum plates were placed in front of the glass cover plate to protect it from radiant heat from inside the furnace. The heating coil around the tube was nowhere nearer than 6 inches to the cover plate, and a good seal was maintained by the use of ordinary stopcock grease.

The resistance coils mounted on the steel mandrils were annealed in the quartz furnace. An oil-sealed pump was used to evacuate the furnace, maintaining a pressure of the order of 0.001 mm of mercury. About an hour was required to bring the furnace to the annealing temperature of 550° C, at which it was maintained for half an hour, after which the power supply was disconnected and the furnace allowed to cool fairly rapidly.

After the annealed resistance coils had been adjusted to the correct lengths, manganin terminal plates were silver-soldered to the ends. Manganin rather than copper plates were used in order to keep the temperature coefficient of resistance as low as possible.

The mounted resistance coils were spaced with many turns of linen thread wound between the turns of wire. All but two of the coils were then impregnated with shellac varnish and baked at 120° C before sealing them in dry air in the containers. In the 2 months immediately after sealing, each resistor, except the two which were not shellacked, decreased in resistance by from 1 to 5 parts in a million, after which the resistance appeared to be stabilized. No change was obtained even during the initial period for the coils that were not shellacked, which suggests that the initial change was from dimensional changes in the shellac.

One of the completed standards is shown in figure 1. The outside diameter of the container is 9 cm and its length 13 cm. The series of holes near the top are just above the double-walled part and are intended to increase the facilities for cooling, and the containers are

[4] Chemical analysis of one lot: Cu 82.2, Mn 13.2, Ni 4.2, Fe 0.3; of second lot, Cu 82.7, Mn 12.1, Ni 4.5, Fe 0.5.

FIGURE 1.—*Double-walled standard resistor.*

left open at the bottom for the same purpose. The terminal posts are entirely of nickel-plated copper, mounted on a hard-rubber top; the distance between the amalgamated current terminals being 16 cm.

III. STABILITY OF RESISTANCE

In the fall of 1933, after all standards had been on hand for at least 2 months, the group of 24 was intercompared, resistance measurements being made to parts in 10 million. Three of the standards were then sent to the International Bureau of Weights and Measures, and since that time four more have been sent to other national laboratories. The remaining 17 standards have been intercompared to parts in 10 million nearly every year since their completion. Two of the standards have changed in resistance by 4 and 8 parts in a million, in the 12 years since their construction and are considered to be of inferior quality. The remaining 15 resistors comprise the group now used for maintenance of the international ohm. The average value of 10 standards is assumed to remain constant with time, and 5 are kept in reserve to replace standards in the group of 10 if any of them should become defective and change in resistance by an unusual amount.

TABLE 1.—*Stability of double-walled resistors in maintenance group*

Standard No.	Change in resistance, in microhms, from 1933 until—										
	1933	1934	1936	1937	1938	1939	1940	1941	1943	1944	1945
68	0	0.1	0.8	0.6	0.7	0.6	0.1	0.2	0.0	0.0	0.1
70	0	.0	−.1	−.7	−.2	−.2	−.4	−.4	−.6	+.2	.3
74	0	−.2	−.1	.0	−.2	−.4	−.6	−.6	.0	−.4	−.7
77	0	−.6	−.8	−1.2	−.8	−1.0	−.9	−1.0	−.7	−1.1	−1.0
78	0	.0	.2	0.1	.4	0.6	.9	0.8	.9	1.0	1.0
81	0	.0	−.4	−.9	−1.0	−1.2	−.9	−.9	−.9	−1.0	−0.9
82	0	−.1	−.1	.0	−0.1	−0.2	−.1	+.0	−.2	−0.2	−.4
84	0	.5	.0	.3	.0	.8	.8	.8	.5	.8	.6
89	0	.0	.5	.0	.1	.1	.0	.0	.1	−.3	+.1
90	0	−.2	−.3	1.3	.8	.8	.6	.7	.7	.5	.5
Average of numerical values without regard to sign											0.56

Table 1 shows how exactly standards in the maintenance group of 10 have kept their relative values during the last 12 years. This table shows the total change, in parts per million, since 1933, calculated on the assumption that their average value has remained constant. Table 2 gives similar data for the 5 reserve standards, measured in terms of the average of the group of 10. Data for the 5 are somewhat incomplete.

TABLE 2.—*Stability of double-walled resistors in reserve group*

Standard No.	Change in resistance, in microhms, from 1933 until—										
	1933	1934	1936	1937	1938	1939	1940	1941	1943	1944	1945
67	0	1.1	0.6	−0.1	−0.2	−0.4	−0.5	−0.6	.....	−0.9	−1.5
69	0	−0.1	.1	.1	.7	1.0	1.2	1.5	1.9	2.0	1.9
72	0	.2	.....	.....	.....	.....	.....	.....	.....	0.6	0.4
73	0	.0	.3	.0	.....	.....	.....	.....	.....	−.8	−.9
83	0	.2	.4	.2	−.2	.....	.....	−1.0	−1.5	−1.9	−2.1

For the 10 resistors now being used in maintaining the international ohm, the maximum net change in 12 years has been 1.0 part per million. The average net change without regard to sign has been 0.56 part per million in 12 years, or at the average yearly rate of about 5 parts in 100 million.

The bridge which has been used for the intercomparison of these resistors has dials that can be set to parts in a million, the next place being obtained from galvanometer deflections. The method of measurement is such that the bridge is relied upon to measure differences in resistance only. The facilities for cooling and the low-temperature coefficients of resistance make possible measurements to 1 or 2 parts in 10 million, when the standards are measured in a well-stirred, thermostatically controlled, oil bath.

With double-walled containers having the resistance coils mounted tightly in contact with one wall, variations in atmospheric pressure tend to expand or compress the walls and thus apply stresses to the coils. To test the change in resistance so produced, three of the double-walled resistors were placed in a closed chamber and measured at about normal and half-normal pressures. The decrease in resistance as the pressure changed from normal to half-normal was found to be from 2 to 4 parts in a million. Assuming the change to be linear, changes in barometric pressure can therefore be expected to produce uncertainties in the resistances of the standards of only 1 or 2 parts in 10 million, which is about the limit of measurement.

On the basis of relative values, standards of this group are about one order better than well-aged standards of the Rosa type. It does not necessarily follow that their average value is more stable. Unfortunately, there has been no satisfactory method of judging the quality of resistors used in maintaining the unit except their ability to maintain relative values. A group that keeps the same relative values could all be changing, but at the same rate.

Before the war, some preliminary results had been obtained from a commutating method of measuring resistance in terms of inductance, which in turn could be calculated from the measured dimensions of a mutual inductor. By this method it was found possible to duplicate measurements of a 1-ohm resistor to 1 part in a million in terms of the calculated mutual inductance. It is expected that such measurement will in the future give data on the stability of groups of resistors over long periods of time. The stability of the inductor can be checked from time to time from its measured dimensions, and it is believed that this can be done to 1 part in a million. Measurements of the resistors in terms of the inductance would then disclose changes as large as 1 or 2 parts in a million in the resistance of the group being used to maintain the unit. It is not expected that resistance can be measured in absolute units to 1 part in a million by this method. It does appear, however, that systematic errors will be sufficiently constant to permit checks of the stability of the unit of resistance to 1 or 2 parts in a million.

WASHINGTON, September 24, 1945.

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